

WHAT'S AHEAD

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14

CHEMICAL KINETICS

14.1 | Factors That Affect Reaction Rates



Chemical reactions take time to occur. Some reactions, such as the rusting of iron, occur relatively slowly, requiring days, months, or years to complete. Others, such as the decomposition of sodium azide, the reaction used to inflate automobile air bags, occur so quickly they are difficult to measure. As chemists, we need to be concerned about the *speed* of chemical reactions as well as the products of those reactions.

The part of chemistry that deals with the speed of a chemical reaction is known as chemical kinetics. It plays an important role in processes as diverse as the production of chemicals on an industrial scale and the decay of radioactive isotopes used in medicine. Chemical kinetics is also useful in providing information about how reactions occur—the order in which chemical bonds are broken and formed during the course of a reaction. Chemical kinetics helps us formulate a reaction mechanism, which is a step-by-step, molecular-level view of the pathway from reactants to products.

The speed at which a chemical reaction occurs is called the **reaction rate**. One mechanism for controlling reaction rate is to adjust the temperature. Reaction rates slow down as the temperature decreases and speed up when the temperature increases. The chemical reactions that govern the metabolism of food, the transport of essential nutrients, and many other important physiological processes in the human body must proceed with the appropriate speeds. To do so, it is essential that our internal body temperature remain relatively constant regardless of the outside temperature. However, not all mammals operate within these strict confines. The body temperatures of animals that hibernate during the cold winter months often drop considerably in order to slow their metabolisms and conserve energy. The most extreme case is the arctic ground squirrel, an animal that hibernates for 7 to 8 months every year. Scientists have measured body temperatures as low as 3 °C in hibernating arctic ground squirrels! At these low temperatures, reaction rates are slowed by several orders of magnitude, which allow the squirrels to hibernate over such long periods.

By the end of this section, you should be able to

- List the factors that affect the rate of chemical reactions.

Four factors affect the rate at which any particular reaction occurs:

1. **Physical state of the reactants.** Reactants must come together to react. The more readily reactant molecules collide with one another, the more rapidly they react. Reactions may broadly be classified as *homogeneous*, involving either all gases or all liquids, or as *heterogeneous*, in which reactants are in different phases. Under heterogeneous conditions, a reaction is limited by the area of contact of the reactants. Thus, heterogeneous reactions that involve solids tend to proceed more rapidly if the surface area of the solid is increased. For example, a medicine in the form of a fine powder dissolves in the stomach and enters the blood more quickly than the same medicine in the form of a tablet.
2. **Reactant concentrations.** Most chemical reactions proceed more quickly if the concentration of one or more reactants is increased. For example, steel wool burns only slowly in air, which contains 20% O₂, but bursts into flame in pure oxygen (Figure 14.1). As reactant concentration increases, the frequency with which the reactant molecules collide increases, leading to increased rates.
3. **Reaction temperature.** Reaction rates generally increase as temperature is increased. The bacterial reactions that spoil milk, for instance, proceed more rapidly at room temperature than at the lower temperature of a refrigerator. Increasing temperature increases the kinetic energies of molecules. As molecules move more rapidly, they collide more frequently and with higher energy, leading to increased reaction rates.
4. **The presence of a catalyst.** Catalysts are agents that increase reaction rates without themselves being used up. They affect the kinds of collisions (and therefore alter the mechanism) that lead to reaction. Catalysts play many crucial roles in living organisms.

On a molecular level, reaction rates depend on the frequency of collisions between molecules. *The greater the frequency of collisions, the higher the reaction rate.* For a collision to lead to a reaction, however, it must occur with sufficient energy to break bonds and with suitable orientation for new bonds to form in the proper locations.

Go Figure

If a heated steel nail were placed in pure O₂, would you expect it to burn as readily as the steel wool does?



Steel wool heated in air (about 20% O₂) glows red-hot but oxidizes to Fe₂O₃ slowly.



Red-hot steel wool in 100% O₂ burns vigorously, forming Fe₂O₃ quickly.

▲ **Figure 14.1** Effect of concentration on reaction rate. The difference in behavior is due to the different concentrations of O₂ in the two environments.

Self-Assessment Exercise

14.1 In a reaction involving molecules in the gas state, how does increasing the partial pressures of the gases affect the reaction rate?

- (a) It will increase the rate
- (b) It will decrease the rate
- (c) The rate will remain unchanged

Exercises

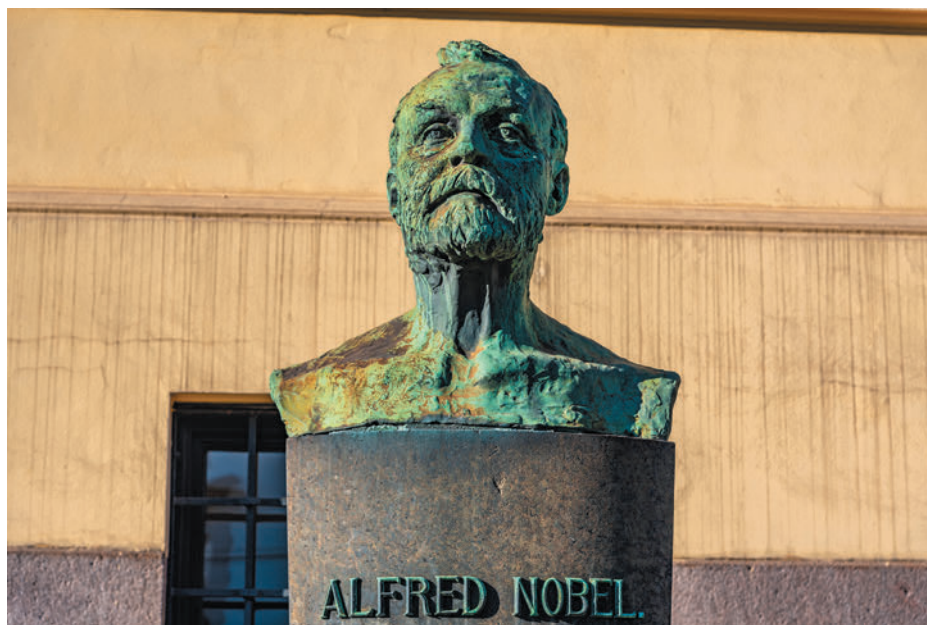
14.2 (a) What is meant by the term *reaction rate*? (b) Name three factors that can affect the rate of a chemical reaction.

(c) Is the rate of disappearance of reactants always the same as the rate of appearance of products?

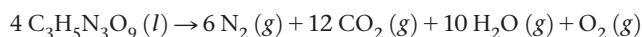
14.1 (a)

Answers to Self-Assessment Exercises

14.2 | Reaction Rates



An explosion is a chemical reaction that occurs very, very fast, coupled with one that is highly exothermic and produces gaseous products. Nitroglycerine fulfills these criteria but is an extremely unstable liquid and very difficult to use.



The Swedish inventor, Alfred Nobel, found that by mixing nitroglycerine with an absorbent solid material such as diatomaceous earth or cellulose, a solid explosive (*dynamite*) was produced and was much easier to handle than nitroglycerine. He had invented the most powerful military explosive to date, but he strongly supported international peace movements. His will stated that his fortune should be used to establish prizes awarding those who 'have conferred the greatest benefit on mankind', including the promotion of peace. The Nobel Prize is probably the most coveted award that a scientist, economist, writer, or peace advocate can receive.

In this section, we introduce reaction rates and by the end of it you should be able to

- Determine the rate of a reaction by measuring the concentration of a reactant or product as a function of time.
- Relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction.

The *speed* of an event is defined as the *change* that occurs in a given *time* interval, which means that whenever we talk about speed, we necessarily bring in the notion of time. For example, the speed of a car is expressed as the change in the car's position over a certain time interval.

Similarly, the speed of a chemical reaction—its reaction rate—is the change in the concentration of reactants or products per unit of time. The units for reaction rate are usually molarity per second (M/s)—that is, the change in concentration measured in molarity divided by a time interval measured in seconds.

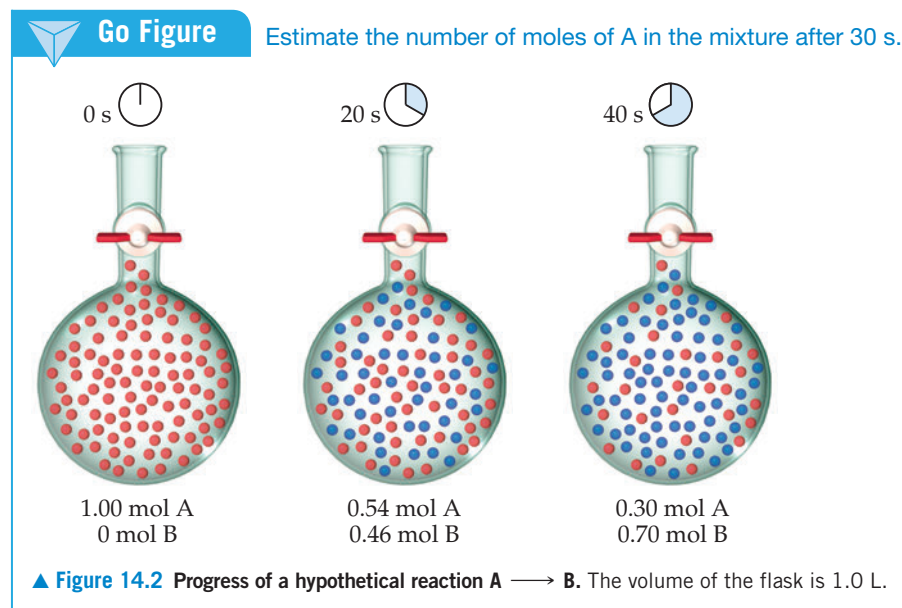
Let's consider the hypothetical reaction $A \longrightarrow B$, depicted in **Figure 14.2**. Each red sphere represents 0.01 mol of A, each blue sphere represents 0.01 mol of B, and the container has a volume of 1.00 L. At the beginning of the reaction, there is 1.00 mol A, so the concentration is $1.00 \text{ mol/L} = 1.00 M$. After 20 s, the concentration of A has fallen to $0.54 M$ and the concentration of B has risen to $0.46 M$. The sum of the concentrations is still $1.00 M$ because 1 mol of B is produced for each mole of A that reacts. After 40 s, the concentration of A is $0.30 M$ and that of B is $0.70 M$.

The rate of this reaction can be expressed either as the rate of disappearance of reactant A or as the rate of appearance of product B. The *average* rate of appearance of B over a particular time interval is given by the change in concentration of B divided by the change in time:

$$\begin{aligned} \text{Average rate of appearance of B} &= \frac{\text{change in concentration of B}}{\text{change in time}} \\ &= \frac{[B] \text{ at } t_2 - [B] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t} \end{aligned} \quad [14.1]$$

We use square brackets around a chemical formula, as in $[B]$, to indicate molarity. The Greek letter delta, Δ , is read “change in” and is always equal to a final value minus an initial value. The average rate of appearance of B over the 20 s interval from the beginning of the reaction ($t_1 = 0 \text{ s}$ to $t_2 = 20 \text{ s}$) is

$$\text{Average rate} = \frac{0.46 M - 0.00 M}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} M/s$$



We could equally well express the reaction rate in terms of the reactant, A. In this case, we would be describing the rate of disappearance of A, which we express as

$$\begin{aligned}\text{Average rate of disappearance of A} &= -\frac{\text{change in concentration of A}}{\text{change in time}} \\ &= -\frac{\Delta[\text{A}]}{\Delta t}\end{aligned}\quad [14.2]$$

Notice the minus sign in this equation, which we use to indicate that the concentration of A decreases.

By convention, rates are always expressed as positive quantities.

Because [A] decreases, $\Delta[\text{A}]$ is a negative number. The minus sign we put in the equation converts the negative $\Delta[\text{A}]$ to a positive rate of disappearance.

Because one molecule of A is consumed for every molecule of B that forms, the average rate of disappearance of A equals the average rate of appearance of B:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.54\text{ M} - 1.00\text{ M}}{20\text{ s} - 0\text{ s}} = 2.3 \times 10^{-2}\text{ M/s}$$



Sample Exercise 14.1

Calculating an Average Rate of Reaction

From the data in Figure 14.2, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

SOLUTION

Analyze We are given the concentration of A at 20 s (0.54 M) and at 40 s (0.30 M) and asked to calculate the average rate of reaction over this time interval.

Plan The average rate is given by the change in concentration, $\Delta[\text{A}]$, divided by the change in time, Δt . Because A is a reactant, a minus sign is used in the calculation to make the rate a positive quantity.

Solve

$$\begin{aligned}\text{Average rate} &= -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30\text{ M} - 0.54\text{ M}}{40\text{ s} - 20\text{ s}} \\ &= 1.2 \times 10^{-2}\text{ M/s}\end{aligned}$$

Practice Exercise

If the experiment in Figure 14.2 is run for 60 s, 0.16 mol A remain. Which of the following statements is or are true?

- (i) After 60 s there are 0.84 mol B in the flask.
- (ii) The decrease in the number of moles of A from $t_1 = 0\text{ s}$ to $t_2 = 20\text{ s}$ is greater than that from $t_1 = 40\text{ s}$ to $t_2 = 60\text{ s}$.
- (iii) The average rate for the reaction from $t_1 = 40\text{ s}$ to $t_2 = 60\text{ s}$ is $7.0 \times 10^{-3}\text{ M/s}$.
- (a) Only one of the statements is true.
- (b) Statements (i) and (ii) are true.
- (c) Statements (i) and (iii) are true.
- (d) Statements (ii) and (iii) are true.
- (e) All three statements are true.

Change of Rate with Time

Now let's consider the reaction between chlorobutane ($\text{C}_4\text{H}_9\text{Cl}$) and water to form butanol ($\text{C}_4\text{H}_9\text{OH}$) and hydrochloric acid:



Suppose we prepare a 0.1000 M aqueous solution of $\text{C}_4\text{H}_9\text{Cl}$ and then measure the concentration of $\text{C}_4\text{H}_9\text{Cl}$ at various times after time zero (which is the instant at which the reactants are mixed, thereby initiating the reaction). We can use the resulting data, shown in the first two columns of **Table 14.1**, to calculate the average rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ over various time intervals; these rates are given in the third column. Notice that the average rate decreases over each 50 s interval for the first several measurements and continues to decrease over even larger intervals through the remaining measurements. *It is typical for rates to decrease as a reaction*

TABLE 14.1 Rate Data for Reaction of $\text{C}_4\text{H}_9\text{Cl}$ with Water

Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	
100.0	0.0820	1.7×10^{-4}
150.0	0.0741	1.6×10^{-4}
200.0	0.0671	1.4×10^{-4}
300.0	0.0549	1.22×10^{-4}
400.0	0.0448	1.01×10^{-4}
500.0	0.0368	0.80×10^{-4}
800.0	0.0200	0.560×10^{-4}
10,000	0	

proceeds because the concentration of reactants decreases. The change in rate as the reaction proceeds is also seen in a graph of $[\text{C}_4\text{H}_9\text{Cl}]$ versus time (Figure 14.3). Notice how the steepness of the curve decreases with time, indicating a decreasing reaction rate.

Instantaneous Rate

Graphs such as Figure 14.3 that show how the concentration of a reactant or product changes with time allow us to evaluate the **instantaneous rate** of a reaction, which is the rate at a particular instant during the reaction. The instantaneous rate is determined from the slope of the curve at a particular point in time. We have drawn two tangent lines in Figure 14.3, a dashed line running through the point at $t = 0$ s and a solid line running through the point at $t = 600$ s. The slopes of these tangent lines give the instantaneous rates at these two time points.* To determine the instantaneous rate at 600 s, for example, we construct horizontal and vertical lines to form the blue right triangle in Figure 14.3. The slope of the tangent line is the ratio of the height of the vertical side to the length of the horizontal side:

$$\begin{aligned}\text{Instantaneous rate} &= -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.017 - 0.042) \text{ M}}{(800 - 400) \text{ s}} \\ &= 6.3 \times 10^{-5} \text{ M/s}\end{aligned}$$

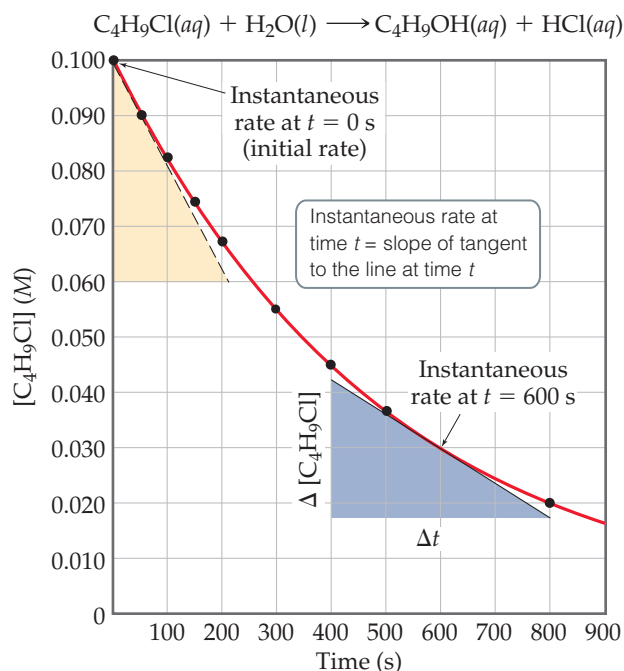
In discussions that follow, the term *rate* means instantaneous rate unless indicated otherwise. The instantaneous rate at $t = 0$ is called the *initial rate* of the reaction. To understand the difference between average and instantaneous rates, imagine you have just driven 160 km in 2.0 h. Your average speed for the trip is 80 km/hr, but your instantaneous speed at any moment during the trip is the speedometer reading at that moment.

*You may wish to review graphical determination of slopes in Appendix A. If you are familiar with calculus, you may recognize that the average rate approaches the instantaneous rate as the time interval approaches zero. This limit, in the notation of calculus, is the negative of the derivative of the curve at time t , $-d[\text{C}_4\text{H}_9\text{Cl}]/dt$.



Go Figure

Does the instantaneous rate increase, decrease, or remain the same as the reaction proceeds?



▲ **Figure 14.3** Concentration of butyl chloride ($\text{C}_4\text{H}_9\text{Cl}$) as a function of time.

Sample Exercise 14.2

Calculating an Instantaneous Rate of Reaction

Using Figure 14.3, calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 0$ s (the initial rate).

SOLUTION

Analyze We are asked to determine an instantaneous rate from a graph of reactant concentration versus time.

Plan To obtain the instantaneous rate at $t = 0$ s, we must determine the slope of the curve at $t = 0$. The tangent is drawn on the graph as the hypotenuse of the tan triangle. The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (which, in the case of this example, is the change in molarity over change in time).

Solve The tangent line falls from $[\text{C}_4\text{H}_9\text{Cl}] = 0.100\text{ M}$ to 0.060 M in the time change from 0 s to 210 s. Thus, the initial rate is

$$\begin{aligned}\text{Rate} &= -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.060 - 0.100)\text{ M}}{(210 - 0)\text{ s}} \\ &= 1.9 \times 10^{-4}\text{ M/s}\end{aligned}$$

Practice Exercise

Which of the following could be the instantaneous rate of the reaction in Figure 14.3 at $t = 1000$ s?

- (a) $1.2 \times 10^{-4}\text{ M/s}$
- (b) $8.8 \times 10^{-5}\text{ M/s}$
- (c) $6.3 \times 10^{-5}\text{ M/s}$
- (d) $2.7 \times 10^{-5}\text{ M/s}$
- (e) More than one of these.

Reaction Rates and Stoichiometry

During our discussion of the hypothetical reaction $\text{A} \longrightarrow \text{B}$, we saw that the stoichiometry requires that the rate of disappearance of A equal the rate of appearance of B. Likewise, the stoichiometry of Equation 14.3 indicates that 1 mol of $\text{C}_4\text{H}_9\text{OH}$ is produced for each mole of $\text{C}_4\text{H}_9\text{Cl}$ consumed. Therefore, the rate of appearance of $\text{C}_4\text{H}_9\text{OH}$ equals the rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$:

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

What happens when the stoichiometric relationships are not one-to-one? For example, consider the reaction $2\text{HI}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$. We can measure either the rate of disappearance of HI or the rate of appearance of either H_2 or I_2 . Because 2 mol of HI disappears for each mole of H_2 or I_2 that forms, the rate of disappearance of HI is *twice* the rate of appearance of either H_2 or I_2 . How do we decide which number to use for the rate of the reaction? Depending on whether we monitor HI, I_2 , or H_2 , the rates can differ by a factor of 2. To fix this problem, we need to take into account the reaction stoichiometry. To arrive at a number for the reaction rate that does not depend on which component we measured, we must divide the rate of disappearance of HI by 2 (its coefficient in the balanced chemical equation):

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

In general, for the reaction



the rate is given by

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t} \quad [14.4]$$

When we speak of the rate of a reaction without specifying a particular reactant or product, we utilize the definition in Equation 14.4.*

*Equation 14.4 does not hold true if substances other than C and D are formed in significant amounts. For example, sometimes intermediate substances build in concentration before forming the final products. In that case, the relationship between the rate of disappearance of reactants and the rate of appearance of products is not given by Equation 14.4. All reactions whose rates we consider in this chapter obey Equation 14.4.

Sample Exercise 14.3

Relating Rates at Which Products Appear and Reactants Disappear



- (a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$?
- (b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

SOLUTION

Analyze We are given a balanced chemical equation and asked to relate the rate of appearance of the product to the rate of disappearance of the reactant.

Plan We can use the coefficients in the chemical equation as shown in Equation 14.4 to express the relative rates of reactions.

Solve

- (a) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

- (b) Solving the equation from part (a) for the rate at which O_3 disappears, $-\Delta[\text{O}_3]/\Delta t$, we have:

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$

Check We can apply a stoichiometric factor to convert the O_2 formation rate to the O_3 disappearance rate:

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \left(6.0 \times 10^{-5} \frac{\text{mol } \text{O}_2/\text{L}}{\text{s}} \right) \left(\frac{2 \text{ mol } \text{O}_3}{3 \text{ mol } \text{O}_2} \right) = 4.0 \times 10^{-5} \frac{\text{mol } \text{O}_3/\text{L}}{\text{s}} = 4.0 \times 10^{-5} \text{ M/s}$$

Practice Exercise

At a certain time in a reaction, substance A is disappearing at a rate of $4.0 \times 10^{-2} \text{ M/s}$, substance B is appearing at a rate of $2.0 \times 10^{-2} \text{ M/s}$, and substance C is appearing at a rate of $6.0 \times 10^{-2} \text{ M/s}$. Which of the following could be the stoichiometry for the reaction being studied?

- (a) $2 \text{A} + \text{B} \longrightarrow 3 \text{C}$ (b) $\text{A} \longrightarrow 2 \text{B} + 3 \text{C}$
 (c) $2 \text{A} \longrightarrow \text{B} + 3 \text{C}$ (d) $4 \text{A} \longrightarrow 2 \text{B} + 3 \text{C}$
 (e) $\text{A} + 2 \text{B} \longrightarrow 3 \text{C}$

Self-Assessment Exercises

- 14.3** In Figure 14.3, order the following three rates from fastest to slowest: (i) The average rate of the reaction between 0 s and 600 s, (ii) the instantaneous rate at $t = 0$ s, and (iii) the instantaneous rate at $t = 600$ s. You should not have to do any calculations.

- (a) Average rate > Rate at $t = 0$ s > Rate at $t = 600$ s
 (b) Rate at $t = 600$ s > Average rate > Rate at $t = 0$ s
 (c) Rate at $t = 0$ s > Average rate > Rate at $t = 600$ s

- 14.4** For the reaction $\text{N}_2\text{O}_4(g) \longrightarrow 2 \text{NO}_2(g)$, how is the rate of disappearance of dinitrogen tetroxide related to the rate of appearance of nitrogen dioxide?

- (a) $\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_4]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{\Delta t}$
 (b) $\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_4]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{\Delta t}$
 (c) $\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_4]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$

Exercises

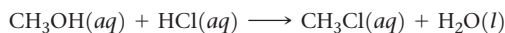
- 14.5** A flask is charged with 0.200 mol of A and allowed to react to form B according to the hypothetical gas-phase reaction $\text{A}(g) \longrightarrow \text{B}(g)$. The following data are collected:

Time (s)	0	50	100	150	200
Moles of A	0.200	0.141	0.100	0.071	0.050

- (a) Calculate the number of moles of B at each time in the table, assuming that A is cleanly converted to B with no intermediates. (b) Calculate the average rate of disappearance of A for each 50 s interval in units of mol/s. (c) Which of the following would be needed to calculate the rate in units of concentration per time: (i) the partial pressure of the gases at

each time, (ii) the temperature, (iii) the volume of the reaction flask, or (iv) the molecular weights of A and B?

- 14.6** The rate of disappearance of HCl was measured for the following reaction:



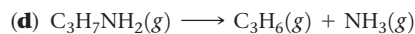
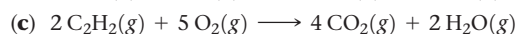
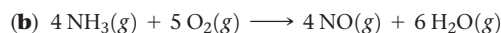
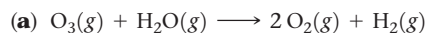
The following data were collected:

Time (min)	[HCl](M)
0.0	1.85
54.0	1.58
107.0	1.36
215.0	1.02
430.0	0.580

- (a) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. (b) Calculate the average rate of reaction for the entire time for the data from $t = 0.0$ min to $t = 430.0$ min. (c) Which is greater,

the average rate between $t = 54.0$ and $t = 215.0$ min, or between $t = 107.0$ and $t = 430.0$ min? (d) Graph [HCl] versus time and determine the instantaneous rates in M/min and M/s at $t = 75.0$ min and $t = 250$ min.

- 14.7** For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product and disappearance of each reactant:



- 14.8** (a) Consider the combustion of ethene, $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$. If the concentration of C_2H_4 is decreasing at the rate of 0.025 M/s, what are the rates of change in the concentrations of CO_2 and H_2O ? (b) The rate of decrease in N_2H_4 partial pressure in a closed reaction vessel from the reaction $\text{N}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$ is 10 kPa per hour. What are the rates of change of NH_3 partial pressure and total pressure in the vessel?

14.3 (c) 14.4 (c)

Answers to Self-Assessment Exercises

14.3 | Concentration and Rate Laws

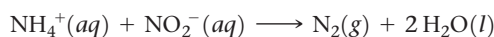


Acid rain results largely from emissions from industry of sulfur dioxide and nitrogen oxide reacting with water in the atmosphere. Coal-fired power stations are a major source of these gases and their emissions increased significantly during the industrial revolution of the nineteenth century. Some statues and buildings, most notably those made of limestone, are sensitive to acidic solutions and erosion of the stone has been accelerated in the modern era as the rain in some regions has become more acidic.

By the end of this section, you should be able to

- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant.
- Determine the rate law and rate constant for a reaction from a series of data.

One way of studying the effect of concentration on reaction rate is to determine the way in which the initial rate of a reaction depends on the initial concentrations. For example, we might study the rate of the reaction



A CLOSER LOOK Using Spectroscopic Methods to Measure Reaction Rates: Beer's Law

A variety of techniques can be used to monitor reactant and product concentration during a reaction, including spectroscopic methods, which rely on the ability of substances to absorb (or emit) light. Spectroscopic kinetic studies are often performed with the reaction mixture in the sample compartment of a *spectrometer*, an instrument that measures the amount of light transmitted or absorbed by a sample at different wavelengths. For kinetic studies, the spectrometer is set to measure the light absorbed at a wavelength characteristic of one of the reactants or products. In the decomposition of $\text{HI}(g)$ into $\text{H}_2(g)$

and $\text{I}_2(g)$, for example, both HI and H_2 are colorless, whereas I_2 is violet. During the reaction, the violet color of the reaction mixture gets more intense as I_2 forms. Thus, visible light of appropriate wavelength can be used to monitor the reaction (Figure 14.4).

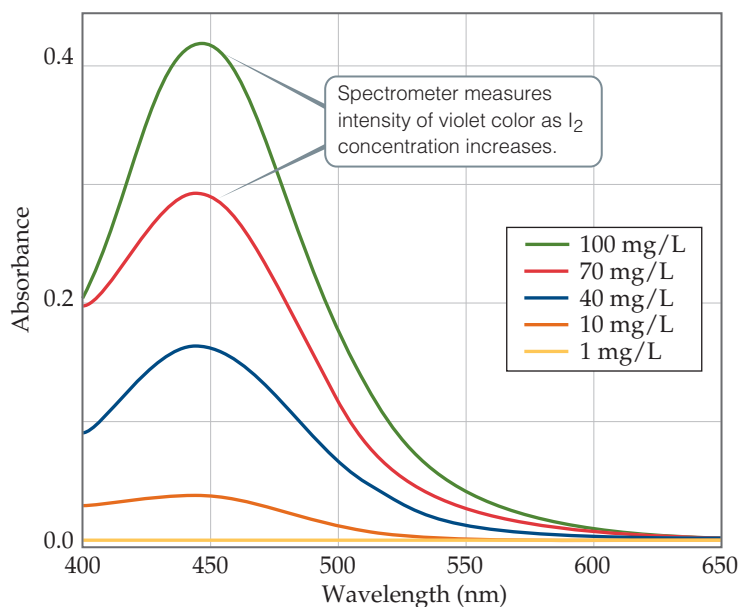
Figure 14.5 shows the components of a spectrometer. The spectrometer measures the amount of light absorbed by the sample by comparing the intensity of the light emitted from the light source with the intensity of the light transmitted through the sample, for various wavelengths. As the concentration of I_2 increases and its color becomes more intense, the amount of light absorbed by the reaction mixture increases, as Figure 14.4 shows, causing less light to reach the detector.

How can we relate the amount of light detected by the spectrometer to the concentration of a species? A relationship called *Beer's law* gives us a direct route to the information we seek. Beer's law connects the amount of light absorbed to the concentration of the absorbing substance:

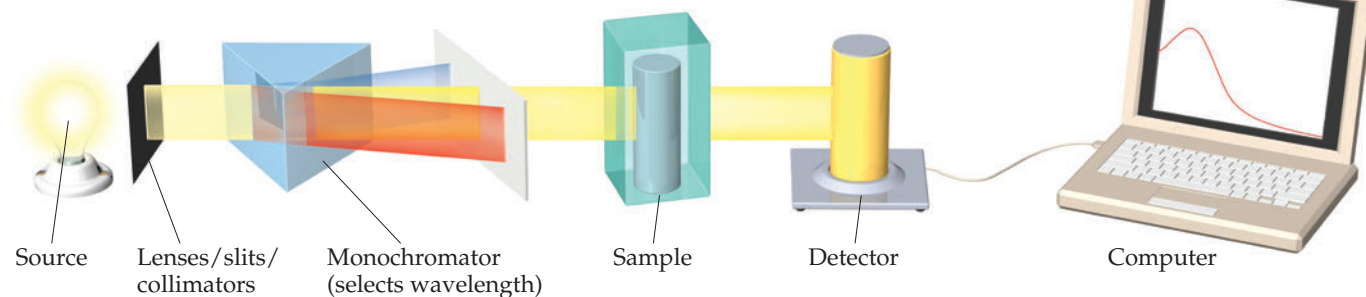
$$A = \epsilon lc \quad [14.5]$$

In this equation, A is the measured absorbance, ϵ is the extinction coefficient (a characteristic of the substance being monitored at a given wavelength of light), l is the path length through which the light passes, and c is the molar concentration of the absorbing substance. Thus, the concentration is directly proportional to absorbance. Many chemical and pharmaceutical companies routinely use Beer's law to calculate the concentration of purified solutions of the compounds that they make. In the laboratory portion of your course, you may very well perform one or more experiments in which you use Beer's law to relate absorption of light to concentration.

Related Exercises: 14.111, 14.112, Design an Experiment



▲ Figure 14.4 Visible spectra of I_2 at different concentrations.



▲ Figure 14.5 Components of a spectrometer.

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

by measuring the concentration of NH_4^+ or NO_2^- as a function of time or by measuring the volume of N_2 collected as a function of time. Because the stoichiometric coefficients on NH_4^+ , NO_2^- , and N_2 are the same, all of these rates are the same.

Table 14.2 shows that changing the initial concentration of either reactant changes the initial reaction rate. If we double $[\text{NH}_4^+]$ while holding $[\text{NO}_2^-]$ constant, the rate doubles (compare experiments 1 and 2). If we increase $[\text{NH}_4^+]$ by a factor of 4 but leave $[\text{NO}_2^-]$ unchanged (experiments 1 and 3), the rate changes by a factor of 4, and so forth. These results indicate that the initial reaction rate is proportional to $[\text{NH}_4^+]$. When $[\text{NO}_2^-]$ is similarly varied while $[\text{NH}_4^+]$ is held constant, the rate is affected in the same manner. Thus, the rate is also directly proportional to the concentration of $[\text{NO}_2^-]$.

We express the way in which the rate depends on the reactant concentrations by the equation

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-] \quad [14.6]$$

An equation such as Equation 14.6, which shows how the rate depends on reactant concentrations, is called a **rate law**. For the general reaction



the rate law generally has the form

$$\text{Rate} = k[A]^m[B]^n \quad [14.7]$$

Notice that only the concentrations of the reactants generally appear in the rate law. The constant k is called the **rate constant**. The magnitude of k changes with temperature and therefore determines how temperature affects rate, as we will see in Section 14.5. The exponents m and n are typically small whole numbers, whose values are not necessarily equal to the coefficients a and b from the balanced equation. As we will learn shortly, if we know m and n for a reaction, we can gain great insight into the individual steps that occur during the reaction.

Once we know the rate law for a reaction and the reaction rate for a set of reactant concentrations, we can calculate the value of k . For example, using the values for experiment 1 in Table 14.2, we can substitute into Equation 14.6:

$$\begin{aligned} 5.4 \times 10^{-7} M/s &= k(0.0100 M)(0.200 M) \\ k &= \frac{5.4 \times 10^{-7} M/s}{(0.0100 M)(0.200 M)} = 2.7 \times 10^{-4} M^{-1}s^{-1} \end{aligned}$$

You should verify that this same value of k is obtained using any of the other experimental results in Table 14.2.

Once we have both the rate law and the k value for a reaction, we can calculate the reaction rate for any set of concentrations. For example, using Equation 14.7 with

$k = 2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, $m = 1$, and $n = 1$, we can calculate the rate for $[\text{NH}_4^+] = 0.100 \text{ M}$ and $[\text{NO}_2^-] = 0.100 \text{ M}$:

$$\text{Rate} = (2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1})(0.100 \text{ M})(0.100 \text{ M}) = 2.7 \times 10^{-6} \text{ M/s}$$

Reaction Orders: The Exponents in the Rate Law

The rate law for most reactions has the form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots \quad [14.8]$$

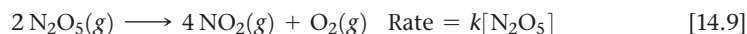
The exponents m and n are called **reaction orders**. For example, consider again the rate law for the reaction of NH_4^+ with NO_2^- :

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

Because the exponent of $[\text{NH}_4^+]$ is 1, the rate is *first order* in NH_4^+ . The rate is also first order in NO_2^- . (The exponent 1 is not shown in rate laws.) The **overall reaction order** is the sum of the orders with respect to each reactant represented in the rate law. Thus, for the reaction between NH_4^+ and NO_2^- the rate law has an overall reaction order of $1 + 1 = 2$, and the reaction is *second order overall*.

The exponents in a rate law indicate how the rate is affected by each reactant concentration. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[\text{NH}_4^+]$ raised to the first power, the rate doubles when $[\text{NH}_4^+]$ doubles, triples when $[\text{NH}_4^+]$ triples, and so forth. Doubling or tripling $[\text{NO}_2^-]$ likewise doubles or triples the rate. If a rate law is second order with respect to a reactant, $[\text{A}]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple because $[2]^2 = 4$, whereas tripling the concentration causes the rate to increase ninefold: $[3]^2 = 9$.

The following are some additional examples of experimentally determined rate laws:



Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case, as Equations 14.9 and 14.11 show.

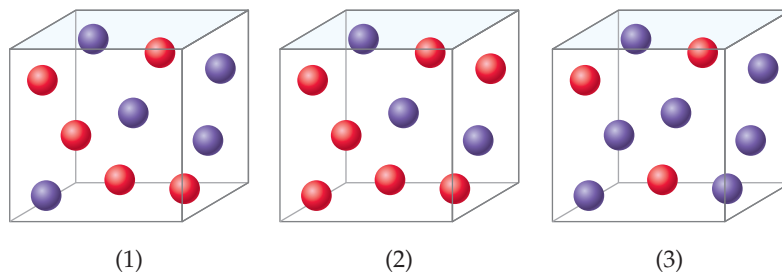
For any reaction, the rate law must be determined experimentally.

In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional (as is the case with Equation 14.11) or even negative.

Sample Exercise 14.4

Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $\text{A} + \text{B} \longrightarrow \text{C}$ for which rate $= k[\text{A}][\text{B}]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



SOLUTION

Analyze We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Continued

Solve Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (Box 2), and the highest is $147k$ (Box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Check Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a larger reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

Practice Exercise

Suppose the rate law for the reaction in this Sample Exercise were $\text{rate} = k[A]^2[B]$. What would be the ordering of the rates for the three mixtures in this Sample Exercise, from slowest to fastest?

- (a) $1 < 2 < 3$
- (b) $1 < 3 < 2$
- (c) $3 < 2 < 1$
- (d) $2 < 1 < 3$
- (e) $3 < 1 < 2$

Magnitudes and Units of Rate Constants

If chemists want to compare reactions to evaluate which ones are relatively fast and which ones are relatively slow, the quantity of interest is the rate constant. A good general rule is that a large value of k ($\sim 10^9$ or higher) means a fast reaction and a small value of k (10 or lower) means a slow reaction.

The units of the rate constant depend on the overall reaction order of the rate law. In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, in our usual units of molarity for concentration and seconds for time, we have

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{M^2} = M^{-1}s^{-1}$$

Sample Exercise 14.5

Determining Reaction Orders and Units for Rate Constants

- (a) What are the overall reaction orders for the reactions described in Equations 14.9 and 14.11?
- (b) What are the units of the rate constant for the rate law in Equation 14.9?

SOLUTION

Analyze We are given two rate laws and asked to express (a) the overall reaction order for each and (b) the units for the rate constant for the first reaction.

Plan The overall reaction order is the sum of the exponents in the rate law. The units for the rate constant, k , are found by using the normal units for rate (M/s) and concentration (M) in the rate law and applying algebra to solve for k .

Solve

- (a) The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.11 is first order in $CHCl_3$ and one-half order in Cl_2 . The overall reaction order is three halves.
- (b) For the rate law for Equation 14.9, we have

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

so

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{M/s}{M} = s^{-1}$$

Note that if the reaction order changes, the units of the rate constant change.

Practice Exercise

Which of the following are the units of the rate constant for Equation 14.11?

- (a) $M^{-1/2}s^{-1}$ (b) $M^{-1/2}s^{-1/2}$ (c) $M^{1/2}s^{-1}$ (d) $M^{-3/2}s^{-1}$ (e) $M^{-3/2}s^{-1/2}$

Using Initial Rates to Determine Rate Laws

We have seen that the rate law for most reactions has the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

Thus, the task of determining the rate law becomes one of determining the reaction orders, m and n . In most reactions, the reaction orders are 0, 1, or 2. As noted earlier in this section, we can use the response of the reaction rate to a change in initial concentration to determine the reaction order.

In working with rate laws, it is important to realize that the *rate* of a reaction depends on concentration but the *rate constant* does not. As we will see later in this chapter, the rate constants (and hence the reaction rate) are affected by temperature and by the presence of a catalyst.

Sample Exercise 14.6

Determining a Rate Law from Initial Rate Data

The initial rate of a reaction $A + B \longrightarrow C$ was measured for three different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A](M)	[B](M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (a) the rate law for the reaction, (b) the rate constant, (c) the rate of the reaction when $[A] = 0.050M$ and $[B] = 0.100M$.

SOLUTION

Analyze We are given a table of data that relates concentrations of reactants with initial rates of reaction and asked to determine (a) the rate law, (b) the rate constant, and (c) the rate of reaction for a set of concentrations not listed in the table.

Plan (a) We assume that the rate law has the following form: $\text{Rate} = k[A]^m[B]^n$. We will use the given data to deduce the reaction orders m and n by determining how changes in the concentration change the rate. (b) Once we know m and n , we can use the rate law and one of the sets of data to determine the rate constant k . (c) Upon determining both the rate constant and the reaction orders, we can use the rate law with the given concentrations to calculate rate.

Solve

- (a) If we compare experiments 1 and 2, we see that [A] is held constant and [B] is doubled. Thus, this pair of experiments shows how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[A_1]^m[B_1]^n}{k[A_2]^m[B_2]^n}$$

Inserting values of rate and concentration from the experiments gives:

$$\frac{4.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = \frac{k[0.100 \text{ M}]^m[0.100 \text{ M}]^n}{k[0.100 \text{ M}]^m[0.200 \text{ M}]^n}$$

$$1 = (1/2)^n$$

The only way this equation can be true is if $n = 0$. Therefore, the rate law is zero order in B, which means that the rate is independent of [B].

In experiments 1 and 3, [B] is held constant, so these data allow us to determine the order of the rate law with respect to [A].

$$\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{k[A_1]^m[B_1]^n}{k[A_3]^m[B_3]^n}$$

Inserting values of rate and concentration from the experiments gives:

$$\frac{16.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = \frac{k[0.200 \text{ M}]^m[0.100 \text{ M}]^n}{k[0.100 \text{ M}]^m[0.100 \text{ M}]^n}$$

$$4 = (2)^m$$

Because the rate increases by a factor of four when [A] is doubled, we can conclude that $m = 2$ and the rate law is second order in B.

Combining these results, we arrive at the rate law:

$$\text{Rate} = k[A]^2[B]^0 = k[A]^2$$

Continued

(b) Using the rate law and the data from experiment 1, we have:

$$k = \frac{\text{rate}}{[\text{A}]^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.100 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(c) Using the rate law from part (a) and the rate constant from part (b), we have:

Because [B] is not part of the rate law, it is irrelevant to the rate if there is at least some B present to react with A.

$$\begin{aligned}\text{Rate} &= k[\text{A}]^2 \\ &= (4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.050 \text{ M})^2 \\ &= 1.0 \times 10^{-5} \text{ M/s}\end{aligned}$$

Check A good way to check our rate law is to use the concentrations in experiment 2 or 3 and see if we can correctly calculate the rate. Using data from experiment 3, we have

$$\begin{aligned}\text{Rate} &= k[\text{A}]^2 = (4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.200 \text{ M})^2 \\ &= 1.6 \times 10^{-4} \text{ M/s}\end{aligned}$$

Thus, the rate law correctly reproduces the data, giving both the correct number and the correct units for the rate.

Practice Exercise

Consider the reaction examined in the Sample Exercise, $\text{A} + \text{B} \rightarrow \text{C}$. If the concentration of B is doubled, the rate of disappearance of B _____, whereas if the concentration of A is doubled, the rate of disappearance of B _____.

- (a) does not change; does not change
- (b) increases by a factor of two; increases by a factor of two
- (c) increases by a factor of four; increases by a factor of two
- (d) does not change; increases by a factor of four
- (e) increases by a factor of four; does not change

- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant.
- Determine the rate law and rate constant for a reaction from a series of data.

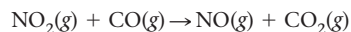
Self-Assessment Exercises

14.9 The experimentally determined rate law for the substitution reaction $(\text{CH}_3)_3\text{CCl} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_3\text{COCH}_3 + \text{HCl}$ is $\text{Rate} = k[(\text{CH}_3)_3\text{CCl}]$.

If the concentration of CH_3OH is doubled, how will the reaction rate change?

- (a) The reaction rate will remain the same
- (b) The reaction rate will double
- (c) The reaction rate will quadruple

14.10 From the given data, determine the rate equation and value of the rate constant for the reaction:



Experiment Number	$[\text{NO}_2] (\text{M})$	$[\text{CO}] (\text{M})$	Initial Rate (M/s)
1	0.10	0.10	0.0050
2	0.40	0.10	0.080
3	0.10	0.20	0.0050

(a) $\text{Rate} = k[\text{NO}_2][\text{CO}]$ where $k = 0.50 \text{ M}^{-1} \text{ s}^{-1}$

(b) $\text{Rate} = k[\text{NO}_2]^2$ where $k = 0.50 \text{ M}^{-1} \text{ s}^{-1}$

(c) $\text{Rate} = k[\text{CO}]^2$ where $k = 0.50 \text{ M}^{-1} \text{ s}^{-1}$

Exercises

14.11 Consider a hypothetical reaction between A, B, and C that is zero order in A, second order in B, and first order in C. (a) Write the rate law for the reaction. (b) How does the rate change when [A] is tripled and the other reactant concentrations are held constant? (c) How does the rate change when [B] is doubled and the other reactant concentrations are held constant? (d) How does the rate change when [C] is tripled and the other reactant concentrations are held constant? (e) By what factor does the rate change when the concentrations of all three reactants are doubled? (f) By what factor does the rate change when the concentrations of all three reactants are cut in half?

14.12 The decomposition reaction of N_2O_5 in tetrachloromethane is $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. The rate law is first order in N_2O_5 . At 55°C the rate constant is $4.12 \times 10^{-3} \text{ s}^{-1}$. (a) Write the rate law for the reaction. (b) What is the rate of reaction when $[\text{N}_2\text{O}_5] = 0.050 \text{ M}$? (c) What happens to the rate when the concentration of N_2O_5 is tripled to 0.150 M ? (d) What happens to the rate when the concentration of N_2O_5 is reduced by 10% to 0.045 M ?

14.13 The reaction between bromoethane ($\text{C}_2\text{H}_5\text{Br}$) and hydroxide ion in ethanol at 330 K , $\text{C}_2\text{H}_5\text{Br}(\text{alc}) + \text{OH}^-(\text{alc}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{Br}^-(\text{alc})$, is first order each in bromoethane and hydroxide ion. When $[\text{C}_2\text{H}_5\text{Br}]$ is 0.0477 M and $[\text{OH}^-]$

is 0.100 M , the rate of disappearance of bromoethane is $1.7 \times 10^{-7}\text{ M/s}$. (a) What is the value of the rate constant? (b) What are the units of the rate constant? (c) How would the rate of disappearance of bromoethane change if the solution were diluted by adding an equal volume of pure ethanol to the solution?

- 14.14** The reaction $2\text{ClO}_2(aq) + 2\text{OH}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)$ was studied with the following results:

Experiment	$[\text{ClO}_2]\text{ (M)}$	$[\text{OH}^-]\text{ (M)}$	Initial Rate (M/s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

(a) Determine the rate law for the reaction. (b) Calculate the rate constant with proper units. (c) Calculate the rate when $[\text{ClO}_2] = 0.100\text{ M}$ and $[\text{OH}^-] = 0.050\text{ M}$.

- 14.15** The following data were collected for the rate of disappearance of NO in the reaction $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$:

Experiment	$[\text{NO}]\text{ (M)}$	$[\text{O}_2]\text{ (M)}$	Initial Rate (M/s)
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0125	5.64×10^{-2}
3	0.0252	0.0250	1.13×10^{-1}

(a) What is the rate law for the reaction? (b) What are the units of the rate constant? (c) What is the average

value of the rate constant calculated from the three data sets? (d) What is the rate of disappearance of NO when $[\text{NO}] = 0.0750\text{ M}$ and $[\text{O}_2] = 0.0100\text{ M}$? (e) What is the rate of disappearance of O_2 at the concentrations given in part (d)?

- 14.16** Consider the reaction of peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$) with iodide ion (I^-) in aqueous solution:



At a particular temperature, the initial rate of disappearance of $\text{S}_2\text{O}_8^{2-}$ varies with reactant concentrations in the following manner:

Experiment	$[\text{S}_2\text{O}_8^{2-}]\text{ (M)}$	$[\text{I}^-]\text{ (M)}$	Initial Rate (M/s)
1	0.018	0.036	2.6×10^{-6}
2	0.027	0.036	3.9×10^{-6}
3	0.036	0.054	7.8×10^{-6}
4	0.050	0.072	1.4×10^{-5}

(a) Determine the rate law for the reaction and state the units of the rate constant. (b) What is the average value of the rate constant for the disappearance of $\text{S}_2\text{O}_8^{2-}$ based on the four sets of data? (c) How is the rate of disappearance of $\text{S}_2\text{O}_8^{2-}$ related to the rate of disappearance of I^- ? (d) What is the rate of disappearance of I^- when $[\text{S}_2\text{O}_8^{2-}] = 0.025\text{ M}$ and $[\text{I}^-] = 0.050\text{ M}$?

14.9 (a) 14.10 (b)

Answers to Self-Assessment Exercises

14.4 | The Change of Concentration with Time



The Iron pillar of Delhi dates from the late fourth to early fifth century and was constructed in the reign of King Chandragupta II. Over the course of time, it has shown great resistance to corrosion, attracting the attention of metallurgists as well as archaeologists. The pillar's endurance is attributed to a natural protective film on the surface of the pillar resulting from a relatively high phosphorous content in the iron. It has outlasted the ravages of time and weather!

At the end of this section, you should be able to

- Apply the integrated form of a rate law to determine the concentration of a reactant at a given time.
- Relate the rate constant for a first order reaction to the reaction half-life.

The rate laws we have examined so far enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. In this section, we will show that rate laws can also be converted into equations that show the relationship between concentrations of reactants or products and time. The mathematics required to accomplish this conversion involves calculus. We do not expect you to be able to perform the calculus operations, but you should be able to use the resulting equations. We will apply this conversion to three of the simplest rate laws: those that are first order overall, those that are second order overall, and those that are zero order overall.

First-Order Reactions

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power. If a reaction of the type $A \longrightarrow \text{products}$ is first order, the rate law is:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

This form of a rate law, which expresses how rate depends on concentration, is called the *differential rate law*. Using the operation from calculus called integration, we see that this relationship can be transformed into an equation known as the *integrated rate law* for a first-order reaction that relates the initial concentration of A, $[A]_0$, to its concentration at any other time t , $[A]_t$:

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln \frac{[A]_t}{[A]_0} = -kt \quad [14.12]$$

The function “ln” in Equation 14.12 is the natural logarithm (Appendix A.2). Equation 14.12 can also be rearranged to

$$\ln[A]_t = -kt + \ln[A]_0 \quad [14.13]$$

Equations 14.12 and 14.13 can be used with any concentration units as long as the units are the same for both $[A]_t$ and $[A]_0$. When dealing with gases, we can use partial pressure as a concentration in Equations 14.12 and 14.13. This substitution follows from the fact that the ideal gas law (see Section 10.4) dictates that at constant temperature the pressure is directly proportional to the concentration (n/V).

For a first-order reaction, Equation 14.12 or 14.13 can be used in several ways. Given any three of the following quantities, we can solve for the fourth: k , t , $[A]_0$, and $[A]_t$. Thus, you can use these equations to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time interval required for a given fraction of a sample to react, or (3) the time interval required for a reactant concentration to fall to a certain level.

Sample Exercise 14.7

Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water at 12 °C follows first-order kinetics with a rate constant of 1.45 yr^{-1} . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$. Assume that the temperature of the lake is constant (so that there are no effects of temperature variation on the rate). (a) What is the concentration of the insecticide on June 1 of the following year? (b) How long will it take for the insecticide concentration to decrease to $3.0 \times 10^{-7} \text{ g/cm}^3$?

SOLUTION

Analyze We are given the rate constant for a reaction that obeys first-order kinetics, as well as information about concentrations and times, and asked to calculate how much reactant (insecticide) remains after 1 yr. We must also determine the time interval needed to reach a particular insecticide concentration.

Plan In part (a) we are given the rate constant, a period of time, and the initial concentration of the reactant, so we can use Equation 14.13 to determine the concentration of the reactant after 1 year has passed. In part (b) we are given the initial and final concentrations and the rate constant. In this case we can use Equation 14.13 to calculate the time that must pass to reach the desired concentration.

Solve

(a) Substituting the known quantities into Equation 14.13, we have: $\ln[\text{insecticide}]_{t=1 \text{ yr}} = -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7})$

We use the $\ln$ function on a calculator to evaluate the second term on the right [that is, $\ln(5.0 \times 10^{-7})$], giving:

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -1.45 + (-14.51) = -15.96$$

To obtain $[\text{insecticide}]_{t=1 \text{ yr}}$, we use the inverse natural logarithm, or e^x , function on the calculator:

$$[\text{insecticide}]_{t=1 \text{ yr}} = e^{-15.96} = 1.2 \times 10^{-7} \text{ g/cm}^3$$

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(b) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7} \text{ g/cm}^3$, gives:

$$\ln(3.0 \times 10^{-7}) = -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

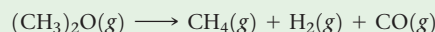
Solving for t gives:

$$\begin{aligned} t &= -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45 \text{ yr}^{-1} \\ &= -(-15.02 + 14.51)/1.45 \text{ yr}^{-1} = 0.35 \text{ yr} \end{aligned}$$

Check In part (a) the concentration remaining after 1.00 yr (that is, $1.2 \times 10^{-7} \text{ g/cm}^3$) is less than the original concentration ($5.0 \times 10^{-7} \text{ g/cm}^3$), as it should be. In (b) the given concentration ($3.0 \times 10^{-7} \text{ g/cm}^3$) is greater than that remaining after 1.00 yr, indicating that the time must be less than a year. Thus, $t = 0.35 \text{ yr}$ is a reasonable answer.

Practice Exercise

The decomposition of dimethyl ether, $(\text{CH}_3)_2\text{O}$, at 510 °C is a first-order process with a rate constant of $6.8 \times 10^{-4} \text{ s}^{-1}$:



If the initial pressure of $(\text{CH}_3)_2\text{O}$ is 18 kPa, what is its pressure after 1420 s?

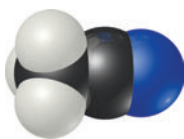
Equation 14.13 can be used to verify whether a reaction is first order and to determine its rate constant. This equation has the form of the general equation for a straight line, $y = mx + b$, in which m is the slope and b is the y -intercept of the line (Appendix A.4):

$$\begin{array}{ccccccc} \ln [A]_t & = & -kt & + & \ln [A]_0 \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

For a first-order reaction, therefore, a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and a y -intercept of $\ln[A]_0$. A reaction that is not first order will not yield a straight line.



Methyl isonitrile



Acetonitrile

▲ **Figure 14.6** The first-order reaction of CH_3NC conversion into CH_3CN .

As an example, consider the conversion of methyl isonitrile (CH_3NC) to its isomer acetonitrile (CH_3CN) (**Figure 14.6**). Because experiments show that the reaction is first order, we can write the rate equation:

$$\ln[\text{CH}_3\text{NC}]_t = -kt + \ln[\text{CH}_3\text{NC}]_0$$

We run the reaction at a temperature at which methyl isonitrile is a gas (199°C), and **Figure 14.7(a)** shows how the pressure of this gas varies with time. **Figure 14.7(b)** shows that a plot of the natural logarithm of the pressure versus time is a straight line. The slope of this line is $-5.1 \times 10^{-5} \text{ s}^{-1}$. (You should verify this for yourself, remembering that your result may vary slightly from ours because of inaccuracies associated with reading the graph.) Because the slope of the line equals $-k$, the rate constant for this reaction equals $5.1 \times 10^{-5} \text{ s}^{-1}$.

Second-Order Reactions

A **second-order reaction** is one for which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power. For simplicity, let's consider reactions of the type $\text{A} \longrightarrow \text{products}$ or $\text{A} + \text{B} \longrightarrow \text{products}$ that are second order in just one reactant, A:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

With the use of calculus, this differential rate law can be used to derive the integrated rate law for second-order reactions:

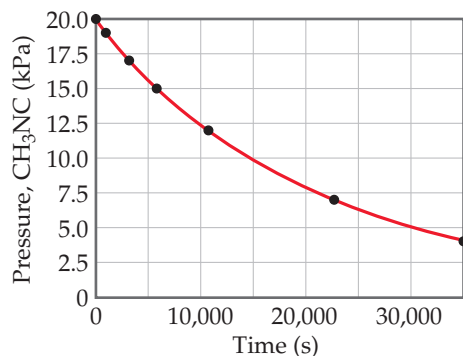
$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0} \quad [14.14]$$

This equation, like Equation 14.13, has four variables, k , t , $[\text{A}]_0$, and $[\text{A}]_t$, and any one of these can be calculated knowing the other three. Equation 14.14 also has the form of a straight line ($y = mx + b$). If the reaction is second order, a plot of $1/[\text{A}]_t$ versus t yields a straight line with slope k and y -intercept $1/[\text{A}]_0$. One way to distinguish between first- and second-order rate laws is to graph both $\ln[\text{A}]_t$ and $1/[\text{A}]_t$ against t . If the $\ln[\text{A}]_t$ plot is linear, the reaction is first order; if the $1/[\text{A}]_t$ plot is linear, the reaction is second order.

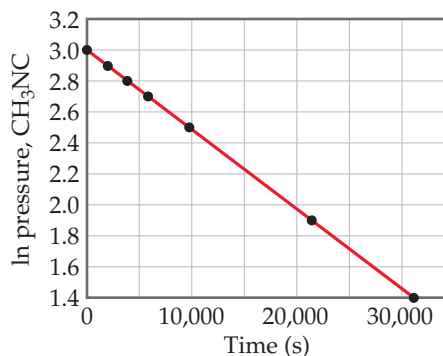


Go Figure

What can you conclude given that the plot of $\ln P$ versus t is linear?



(a)



(b)

▲ **Figure 14.7** Kinetic data for conversion of methyl isonitrile into acetonitrile.

Sample Exercise 14.8

Determining Reaction Order from the Integrated Rate Law

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C, $\text{NO}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$. Is the reaction first or second order in NO_2 ?

Time (s)	$[\text{NO}_2](\text{M})$
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

SOLUTION

Analyze We are given the concentrations of a reactant at various times during a reaction and asked to determine whether the reaction is first or second order.

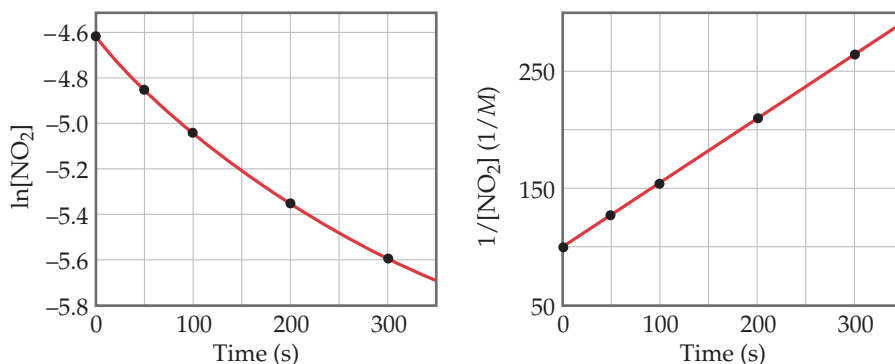
Plan We can plot $\ln[\text{NO}_2]$ and $1/[\text{NO}_2]$ against time. If one plot or the other is linear, we will know the reaction is either first or second order.

Solve

To graph $\ln[\text{NO}_2]$ and $1/[\text{NO}_2]$ against time, we first make the following calculations from the data given:

Time (s)	$[\text{NO}_2](\text{M})$	$\ln[\text{NO}_2]$	$1/[\text{NO}_2] (1/\text{M})$
0.0	0.01000	-4.605	100
50.0	0.00787	-4.845	127
100.0	0.00649	-5.037	154
200.0	0.00481	-5.337	208
300.0	0.00380	-5.573	263

As **Figure 14.8** shows, only the plot of $1/[\text{NO}_2]$ versus time is linear. Thus, the reaction obeys a second-order rate law: $\text{Rate} = k[\text{NO}_2]^2$. From the slope of this straight-line graph, we determine that $k = 0.543 \text{ M}^{-1} \text{ s}^{-1}$ for the disappearance of NO_2 .



▲ **Figure 14.8** Kinetic data for decomposition of NO_2 .

Practice Exercise

For a certain reaction $\text{A} \longrightarrow \text{products}$, a plot of $\ln[\text{A}]$ versus time produces a straight line with a slope of $-3.0 \times 10^{-2} \text{ s}^{-1}$. Which of the following statements is or are true?

- (i) The reaction follows first-order kinetics.
- (ii) The rate constant for the reaction is $3.0 \times 10^{-2} \text{ s}^{-1}$.
- (iii) The initial concentration of $[\text{A}]$ was 1.0 M.

- (a) Only one of the statements is true.
- (b) Statements (i) and (ii) are true.
- (c) Statements (i) and (iii) are true.
- (d) Statements (ii) and (iii) are true.
- (e) All three statements are true.

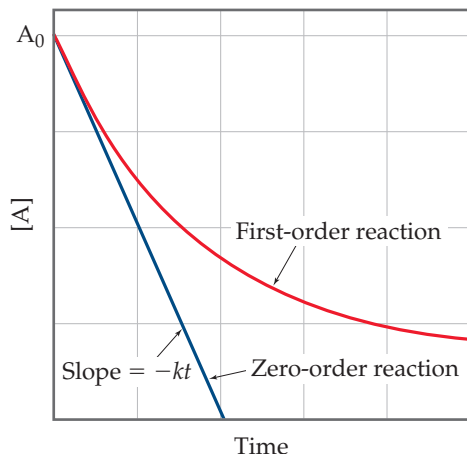
Zero-Order Reactions

We have seen that in a first-order reaction the concentration of a reactant A decreases nonlinearly, as shown by the red curve in **Figure 14.9**. As $[\text{A}]$ declines, the *rate* at which it disappears declines in proportion. A **zero-order reaction** is one in which the rate of disappearance of A is *independent* of $[\text{A}]$. The rate law for a zero-order reaction is

$$\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta t} = k \quad [14.15]$$

Go Figure

At which times during the reaction would you have trouble distinguishing a zero-order reaction from a first-order reaction?



▲ **Figure 14.9** Comparison of first-order and zero-order reactions for the disappearance of reactant A with time.

The integrated rate law for a zero-order reaction is

$$[A]_t = -kt + [A]_0 \quad [14.16]$$

where $[A]_t$ is the concentration of A at time t and $[A]_0$ is the initial concentration. This is the equation for a straight line with vertical intercept $[A]_0$ and slope $-kt$, as shown in the blue curve in Figure 14.9.

The most common type of zero-order reaction occurs when a gas undergoes decomposition on the surface of a solid. If the surface is completely covered by decomposing molecules, the rate of reaction is constant because the number of reacting surface molecules is constant, so long as there is some gas-phase substance left.

Half-Life

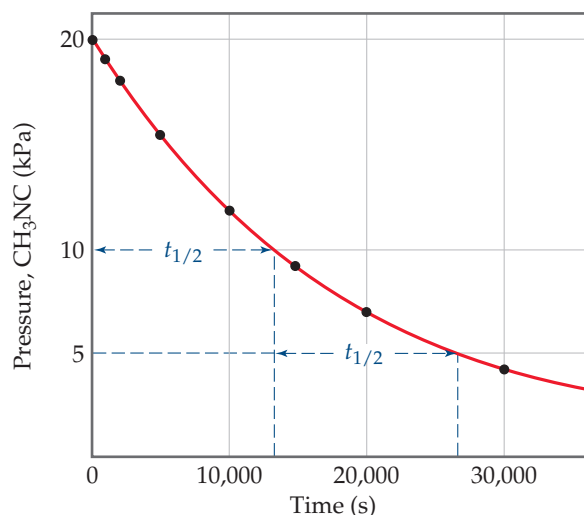
The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach half its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process. A fast reaction has a short half-life.

We can determine the half-life of a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12:

$$\begin{aligned} \ln \frac{\frac{1}{2}[A]_0}{[A]_0} &= -kt_{1/2} \\ \ln \frac{1}{2} &= -kt_{1/2} \\ t_{1/2} &= -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k} \end{aligned} \quad [14.17]$$

From Equation 14.17, we see that $t_{1/2}$ for a first-order rate law does not depend on the initial concentration of any reactant. Consequently, the half-life remains constant throughout the reaction. If, for example, the initial concentration of a reactant is 0.120 M it will be $\frac{1}{2}(0.120\text{ M}) = 0.060\text{ M}$ after one half-life. After one more half-life passes, the concentration will drop to 0.030 M , and so on. Equation 14.17 also indicates that, for a first-order reaction, we can calculate $t_{1/2}$ if we know k and calculate k if we know $t_{1/2}$.

The change in concentration over time for the first-order rearrangement of gaseous methyl isonitrile at 199°C is graphed in Figure 14.10. Because the concentration of this gas is directly proportional to its pressure during the reaction, we have chosen to plot pressure rather than concentration in this graph. The first half-life occurs at $13,600\text{ s}$ (3.78 h). At a time $13,600\text{ s}$ later, the methyl isonitrile pressure (and therefore, concentration) has decreased to half of one-half, or one-fourth, of the initial value.



▲ **Figure 14.10** Kinetic data for the rearrangement of methyl isonitrile to acetonitrile at 199°C , showing the half-life of the reaction.

In a first-order reaction, the concentration of the reactant decreases by one-half in each of a series of regularly spaced time intervals, each interval equal to $t_{1/2}$.

The half-life for second-order and other reactions depends on reactant concentrations and therefore changes as the reaction progresses. We obtained Equation 14.17 for the half-life for a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12. We find the half-life of a second-order reaction by making the same substitutions into Equation 14.14:

$$\begin{aligned} \frac{1}{\frac{1}{2}[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned} \quad [14.19]$$

In this case, the half-life depends on the initial concentration of reactant—the lower the initial concentration, the longer the half-life.

CHEMISTRY PUT TO WORK Bromomethane in the Atmosphere

The compounds known as chlorofluorocarbons (CFCs) are well-known agents responsible for the destruction of Earth's protective ozone layer. Another simple molecule that has the potential to destroy the stratospheric ozone layer is bromomethane, CH_3Br (Figure 14.11). Because this substance has a wide range of uses, including antifungal treatment of plant seeds, it has been produced in large quantities in the past (at the height of its production in 1997 about 70 000 tonnes per year worldwide). In the stratosphere, the C—Br bond is broken

through absorption of short-wavelength radiation. The resultant Br atoms then catalyze decomposition of O_3 .

Bromomethane is removed from the lower atmosphere by a variety of mechanisms, including a slow reaction with ocean water:



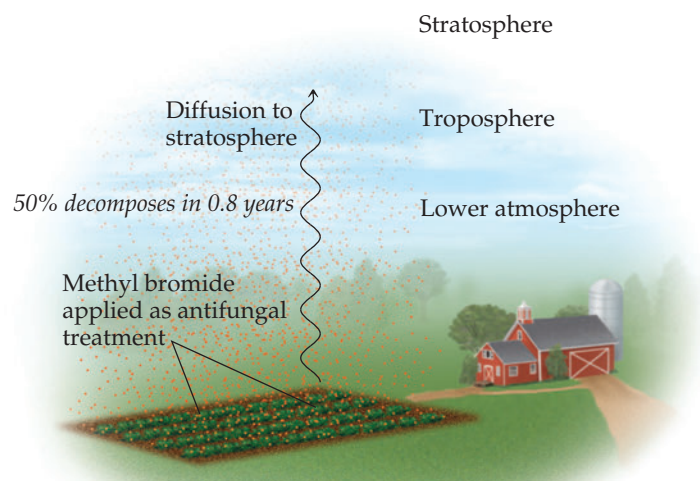
To determine the potential importance of CH_3Br in destruction of the ozone layer, it is important to know how rapidly the reaction in Equation 14.18 and all other reactions remove CH_3Br from the lower atmosphere before it can diffuse into the stratosphere.

The average lifetime of CH_3Br in Earth's lower atmosphere is difficult to measure because the conditions that exist in the atmosphere are too complex to be simulated in the laboratory. Instead, scientists analyzed nearly 4000 atmospheric samples collected above the Pacific Ocean for the presence of several trace organic substances, including bromomethane. From these measurements, it was possible to estimate the *atmospheric residence time* for CH_3Br .

The atmospheric residence time is related to the half-life for CH_3Br in the lower atmosphere, assuming CH_3Br decomposes by a first-order process. From the experimental data, the half-life for bromomethane in the lower atmosphere is estimated to be 0.8 ± 0.1 yr. That is, a collection of CH_3Br molecules present at any given time will, on average, be 50% decomposed after 0.8 yr, 75% decomposed after 1.6 yr, and so on. A half-life of 0.8 yr, while comparatively short, is still sufficiently long so that CH_3Br contributes significantly to the destruction of the ozone layer.

In 1997 an international agreement was reached to phase out use of bromomethane in developed countries by 2005. Although exemptions for critical agricultural use have been granted, global consumption in 2013 was only 3% of the levels seen in the early 1990s.

Related Exercise: 14.131



▲ Figure 14.11 Distribution and fate of methyl bromide in Earth's atmosphere.

Sample Exercise 14.9

Determining the Half-Life of a First-Order Reaction

The reaction of $\text{C}_4\text{H}_9\text{Cl}$ with water is a first-order reaction. (a) Use Figure 14.3 to estimate the half-life for this reaction. (b) Use the half-life from (a) to calculate the rate constant.

SOLUTION

Analyze We are asked to estimate the half-life of a reaction from a graph of concentration versus time and then to use the half-life to calculate the rate constant for the reaction.

Plan

- (a) To estimate a half-life, we can select a concentration and then determine the time required for the concentration to decrease to half of that value.
- (b) Equation 14.17 is used to calculate the rate constant from the half-life.

Solve

- (a) From the graph, we see that the initial value of $[\text{C}_4\text{H}_9\text{Cl}]$ is 0.100 M . The half-life for this first-order reaction is the time required for $[\text{C}_4\text{H}_9\text{Cl}]$ to decrease to 0.050 M , which we can read off the graph. This point occurs at approximately 340 s.

- (b) Solving Equation 14.17 for k , we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\text{ s}} = 2.0 \times 10^{-3}\text{ s}^{-1}$$

Check At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 M . Inspection of the graph shows that this is indeed the case.

► Practice Exercise

- (a) Using Equation 14.17, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7.
- (b) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Self-Assessment Exercises

- 14.17** In 1 L of a solution, 10.0 g of substance A remain after three-half-lives of a first order reaction. What was the original amount of substance A before the start of the reaction?
 (a) 3.33 g
 (b) 30.0 g
 (c) 80.0 g
- 14.18** An antibiotic breaks down in the body with a first order rate constant of $k = 1.9 \times 10^{-2} \text{ min}^{-1}$. What is the half-life of the antibiotic?
 (a) 16 min
 (b) 36 min
 (c) 52 min

Exercises

- 14.19** (a) For the generic reaction $A \rightarrow B$ what quantity, when graphed versus time, will yield a straight line for a first-order reaction? (b) How can you calculate the rate constant for a first-order reaction from the graph you made in part (a)?
- 14.20** (a) The gas-phase decomposition of sulfuryl chloride (SO_2Cl_2), $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is first order in SO_2Cl_2 . At 300°C the half-life for this process is two and a half days. What is the rate constant at this temperature? (b) At 400°C the rate constant is 0.19 min^{-1} . What is the half-life at this temperature?
- 14.21** As described in Exercise 14.20, the decomposition of sulfuryl chloride (SO_2Cl_2) is a first-order process. The rate constant for the decomposition at 660 K is $4.5 \times 10^{-2} \text{ s}^{-1}$. (a) If we begin with an initial SO_2Cl_2 pressure of 60 kPa , what is the partial pressure of this substance after 60 s ? (b) At what time will the partial pressure of SO_2Cl_2 decline to one-tenth its initial value?
- 14.22** From the following data for the second-order gas-phase decomposition of HI at 430°C , calculate the second-order rate constant and half-life for the reaction:

Time (s)	$[\text{HI}]/\text{mol dm}^{-3}$
0	1
100	0.89
200	0.8
300	0.72
400	0.66

- 14.23** Consider the data presented in Exercise 14.5. (a) Determine whether the reaction is first order or second order. (b) What is the rate constant? (c) What is the half-life?
- 14.24** Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), commonly known as table sugar, reacts in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the formula $\text{C}_6\text{H}_{12}\text{O}_6$. At 23°C and in 0.5 M HCl , the following data were obtained for the disappearance of sucrose:

Time (min)	$[\text{C}_{12}\text{H}_{22}\text{O}_{11}] (\text{M})$
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

- (a) Is the reaction first order or second order with respect to $[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$? (b) What is the rate constant? (c) Using this rate constant, calculate the concentration of sucrose at 39, 80, 140, and 210 min if the initial sucrose concentration was 0.316 M and the reaction were zero order in sucrose.

14.5 | Temperature and Rate



The rates of most chemical reactions increase as the temperature rises. For example, dough rises faster at room temperature than when refrigerated, and plants grow more rapidly in warm weather than in cold. We can see the effect of temperature on reaction rate by observing a chemiluminescence reaction (one that produces light), such as that in Cyalume® light sticks (Figure 14.12).

By the end of this section, you should be able to

- Explain how the activation energy affects a rate and be able to use the Arrhenius equation.

How is this experimentally observed temperature effect reflected in the rate law? The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature. For example, let's reconsider the first-order reaction we saw in Figure 14.6 namely, $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$. Figure 14.13 shows the rate constant for this reaction as a function of temperature. The rate constant and, hence, the rate of the reaction increase rapidly with temperature, approximately doubling for each 10 °C rise.

The Collision Model

Reaction rates are affected both by reactant concentrations and by temperature. The **collision model**, based on the kinetic-molecular theory, accounts for both of these effects at the molecular level. The central idea of the collision model is that molecules must collide to react. The greater the number of collisions per second, the greater the reaction rate. As reactant concentration increases, therefore, the number of collisions increases, leading to an increase in reaction rate. According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, both of which increase the reaction rate.

For a reaction to occur, though, more is required than simply a collision—it must be the right kind of collision. For most reactions, in fact, only a tiny fraction of collisions leads to a reaction. For example, in a mixture of H_2 and I_2 at ordinary temperatures and pressures, each molecule undergoes about 10^{10} collisions per second. If every collision between H_2 and I_2 resulted in the formation of HI , the reaction would be over in much less than a second. Instead, at room temperature the reaction proceeds very slowly because only about one in every 10^{13} collisions produces a reaction. What keeps the reaction from occurring more rapidly?

The Orientation Factor

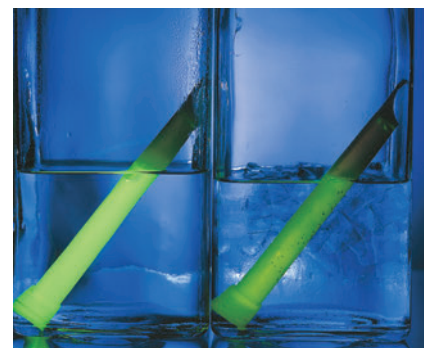
In most reactions, collisions between molecules result in a chemical reaction only if the molecules are oriented in a certain way when they collide. The relative orientations of the molecules during collision determine whether the atoms are suitably positioned to form new bonds. For example, consider the reaction



which takes place if the collision brings Cl atoms together to form Cl_2 , as shown in the top panel of Figure 14.14. In contrast, in the collision shown in the lower panel, the two Cl atoms are not colliding directly with one another, and no products are formed.

Activation Energy

Molecular orientation is not the only factor influencing whether a molecular collision will produce a reaction. In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy to react. According to the collision model, this energy comes from the kinetic energies of the colliding molecules. Upon collision, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. That is, the kinetic energy is used to change the potential energy



Hot water

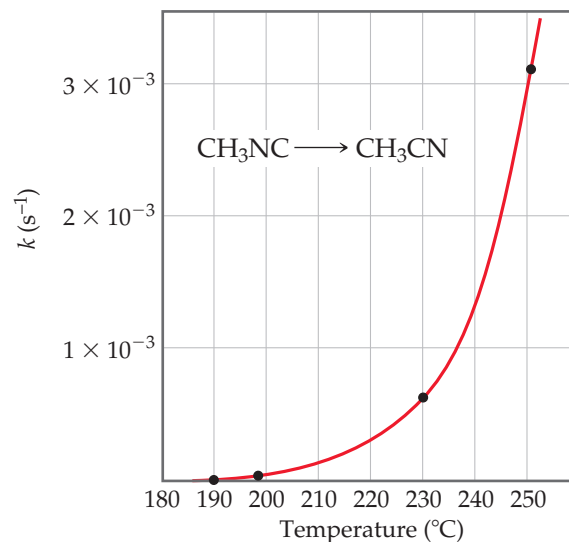
Cold water

▲ **Figure 14.12** Temperature affects the rate of the chemiluminescence reaction in light sticks: The chemiluminescent reaction occurs more rapidly in hot water, and more light is produced.

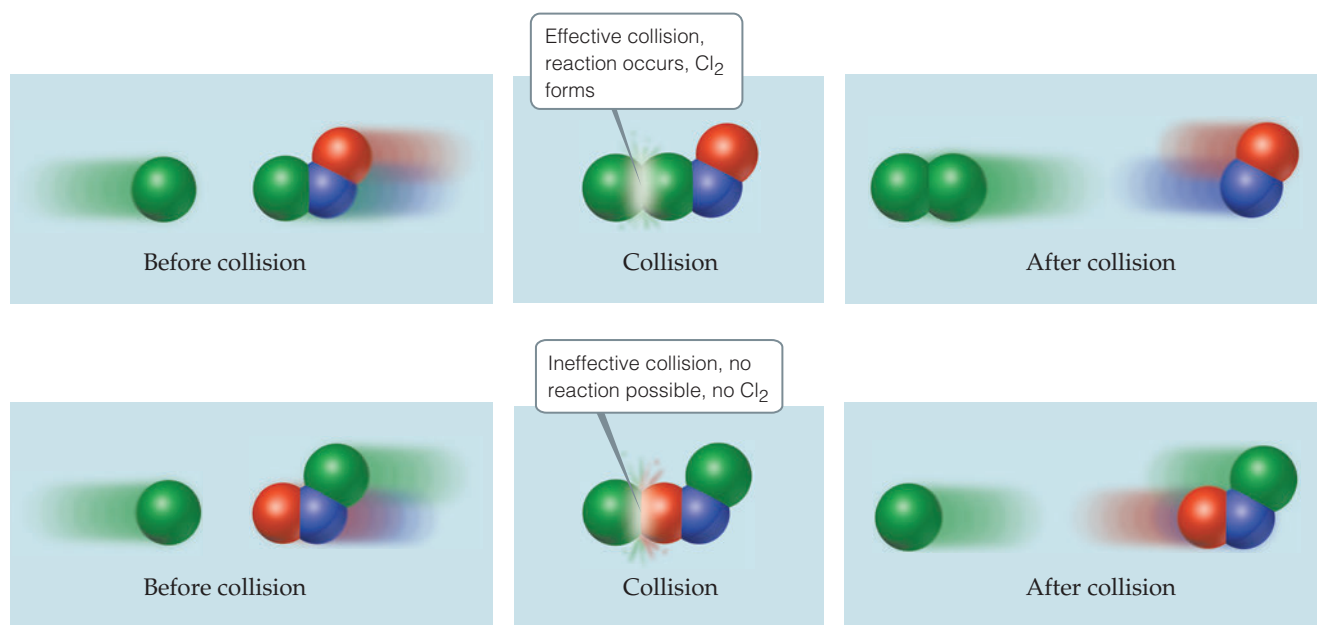


Go Figure

Would you expect this curve to eventually go back down to lower values? Why or why not?



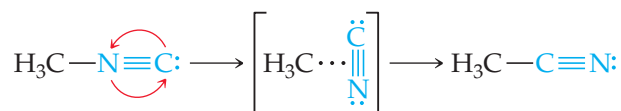
▲ **Figure 14.13** Temperature dependence of the rate constant for methyl isonitrile conversion to acetonitrile. The four points indicated are used in Sample Exercise 14.11.



▲ Figure 14.14 Molecular collisions may or may not lead to a chemical reaction between Cl and NOCl.

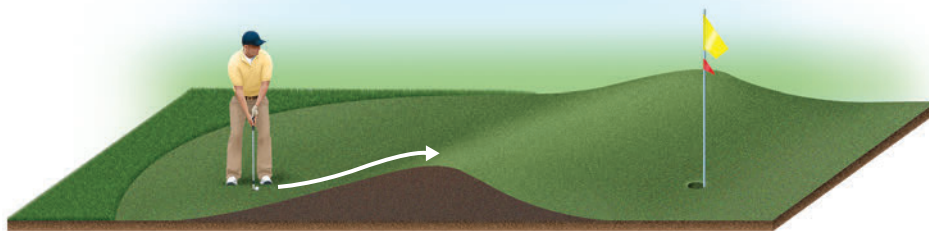
of the molecule. If molecules are moving too slowly—in other words, with too little kinetic energy—they merely bounce off one another without changing. The minimum energy required to initiate a chemical reaction is called the **activation energy**, E_a , and its value varies from reaction to reaction.

The situation during reactions is analogous to that shown in Figure 14.15. The golfer hits the ball to make it move over the hill in the direction of the cup. The hill is a *barrier* between ball and cup. To reach the cup, the player must impart enough kinetic energy with the putter to move the ball to the top of the barrier. If he does not impart enough energy, the ball will roll partway up the hill and then back down toward him. In the same way, molecules require a certain minimum energy to break existing bonds during a chemical reaction. We can think of this minimum energy as an *energy barrier*. In the rearrangement of methyl isonitrile to acetonitrile, for example, we might imagine the reaction passing through an intermediate state in which the $\text{N}\equiv\text{C}$ portion of the methyl isonitrile molecule is sideways:



Go Figure

Which of the following determines how hard the golfer must strike the ball: the difference in elevation between the ball and the hole or between the ball and the top of the barrier?



▲ Figure 14.15 Energy is needed to overcome a barrier between initial and final states.

Figure 14.16 shows that energy must be supplied to stretch the bond between the H_3C group and the $\text{N}\equiv\text{C}$ group to allow the $\text{N}\equiv\text{C}$ group to rotate. After the $\text{N}\equiv\text{C}$ group has twisted sufficiently, the $\text{C}-\text{C}$ bond begins to form, and the energy of the molecule drops. Thus, the barrier to formation of acetonitrile represents the energy necessary to force the molecule through the relatively unstable intermediate state, analogous to forcing the ball in Figure 14.15 over the hill. The difference between the energy of the starting molecule and the highest energy along the reaction pathway is the activation energy, E_a . The molecule having the arrangement of atoms shown at the top of the barrier is called either the **activated complex** or the **transition state**.

The conversion of $\text{H}_3\text{C}-\text{N}\equiv\text{C}$ to $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ is exothermic. Figure 14.16 therefore shows the product as having a lower energy than the reactant. The energy change for the reaction, ΔE , has no effect on reaction rate, however.

The rate constant depends on the magnitude of E_a ; generally, the lower the value of E_a is, the larger the rate constant and the faster the reaction.

Notice that the reverse reaction is endothermic. The activation energy for the reverse reaction is equal to the energy that must be overcome if approaching the barrier from the right: $\Delta E + E_a$. Thus, to reach the activated complex for the reverse reaction requires more energy than for the forward reaction—for this reaction, there is a larger barrier to overcome going from right to left than from left to right.

Any particular methyl isonitrile molecule acquires sufficient energy to overcome the energy barrier through collisions with other molecules. Recall from the kinetic-molecular theory of gases that, at any instant, gas molecules are distributed in energy over a wide range. Figure 14.17 shows the distribution of kinetic energies for two temperatures, comparing them with the minimum energy needed for reaction, E_a . At the higher temperature a much greater fraction of the molecules have kinetic energy greater than E_a , which leads to a greater rate of reaction.

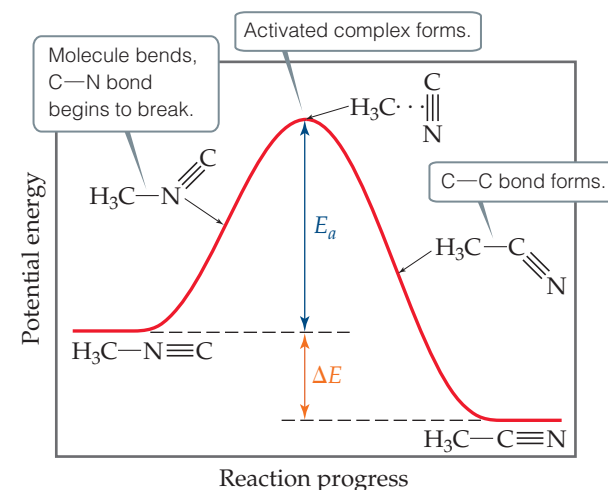
For a collection of molecules in the gas phase, the fraction of molecules that have kinetic energy equal to or greater than E_a is given by the expression

$$f = e^{-E_a/RT} \quad [14.20]$$

In this equation, R is the gas constant (18.314 J/mol K) and T is the absolute temperature. To get an idea of the magnitude of f , let's suppose that E_a is 100 kJ/mol , a value typical of many reactions, and that T is 300 K . The calculated value of f is 3.9×10^{-18} , an extremely small

Go Figure

How does the energy needed to overcome the energy barrier compare with the overall change in energy for this reaction?

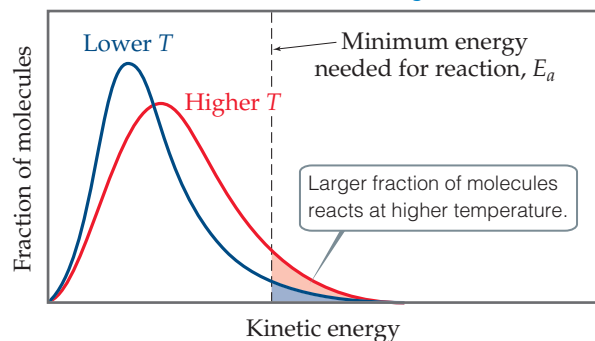


▲ Figure 14.16 Energy profile for conversion of methyl isonitrile (H_3CNC) to its isomer acetonitrile (H_3CCN).



Go Figure

What would the curve look like for a temperature higher than that for the red curve in the figure?



▲ Figure 14.17 The effect of temperature on the distribution of kinetic energies of molecules in a sample.

number! At 320 K, $f = 4.7 \times 10^{-17}$. Thus, only a 20° increase in temperature produces a more than tenfold increase in the fraction of molecules possessing at least 100 kJ/mol of energy.

The Arrhenius Equation

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear (Figure 14.13). He found that most reaction-rate data obeyed an equation based on (a) the fraction of molecules possessing energy E_a or greater, (b) the number of collisions per second, and (c) the fraction of collisions that have the appropriate orientation. These three factors are incorporated into the **Arrhenius equation**:

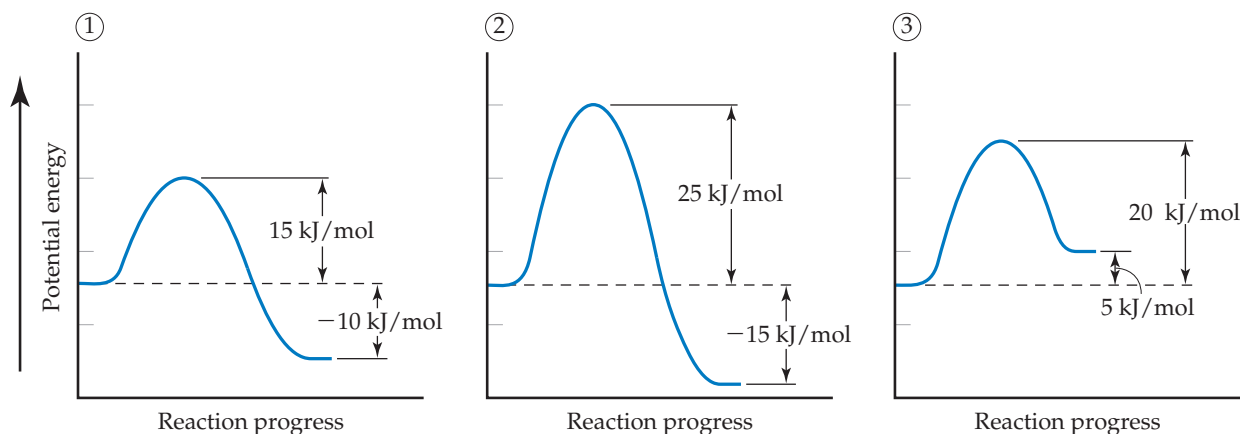
$$k = Ae^{-E_a/RT} \quad [14.21]$$

In this equation, k is the rate constant, E_a is the activation energy, R is the gas constant (18.314 J/mol K), and T is the absolute temperature. The **frequency factor**, A , is constant, or nearly so, as temperature is varied. This factor is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction.* As the magnitude of E_a increases, k decreases because the fraction of molecules that possess the required energy is smaller. Thus, at fixed values of T and A , *the rate constant decreases as E_a increases*.

Sample Exercise 14.10

Activation Energies and Speeds of Reaction

Consider a series of reactions having these energy profiles:



Rank the forward rate constants from smallest to largest assuming all three reactions have nearly the same value for the frequency factor A .

SOLUTION

The lower the activation energy, the larger the rate constant and the faster the reaction. The value of ΔE does not affect the value of the rate constant. Hence, the order of the rate constants is $2 < 3 < 1$.

Practice Exercise

Which of the following changes *always* leads to an increase in the rate constant for a reaction:

- (i) Decreasing the temperature
- (ii) Decreasing the activation energy
- (iii) Making the value of ΔE more negative
- (a) Only one—(i), or (ii), or (iii)—increases the reaction rate.
- (b) (i) and (ii)
- (c) (i) and (iii)
- (d) (ii) and (iii)
- (e) All three—(i), (ii), and (iii)—increase the reaction rate.

*Because collision frequency increases with temperature, A also has some temperature dependence, but this dependence is much smaller than the exponential term. Therefore, A is considered to be approximately constant.

Determining the Activation Energy

We can calculate the activation energy for a reaction by manipulating the Arrhenius equation. Taking the natural log of both sides of Equation 14.21, we obtain

$$\begin{aligned}\ln k &= \ln A e^{-E_a/RT} \\ \ln k &= \ln e^{-E_a/RT} + \ln A \\ \ln k &= -\frac{E_a}{RT} + \ln A\end{aligned}\quad [14.22]$$

$\begin{array}{ccc} \updownarrow & \updownarrow & \updownarrow \\ y & = & mx + b \end{array}$

which has the form of the equation for a straight line. A graph of $\ln k$ versus $1/T$ is a line with a slope equal to $-E_a/R$ and a y -intercept equal to $\ln A$. Thus, the activation energy can be determined by measuring k at a series of temperatures, graphing $\ln k$ versus $1/T$, and calculating E_a from the slope of the resultant line.

We can also use Equation 14.22 to evaluate E_a in a nongraphical way if we know the rate constant of a reaction at two or more temperatures. For example, suppose that at two different temperatures T_1 and T_2 a reaction has rate constants k_1 and k_2 . For each condition, we have

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

Assuming temperature-dependent changes in the frequency factor A are negligible, we can simplify to obtain

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [14.23]$$

Equation 14.23 provides a convenient way to calculate a rate constant k_1 at some temperature T_1 when we know the activation energy and the rate constant k_2 at some other temperature T_2 .



Sample Exercise 14.11

Determining the Activation Energy

The table at right shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data points in Figure 14.13):

- From these data, calculate the activation energy for the reaction.
- What is the value of the rate constant at 430.0 K?

Temperature (°C)	k (s ⁻¹)
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

SOLUTION

Analyze We are given rate constants, k , measured at several temperatures and asked to determine the activation energy, E_a , and the rate constant, k , at a particular temperature.

Plan We can obtain E_a from the slope of a graph of $\ln k$ versus $1/T$. Once we know E_a , we can use Equation 14.23 together with the given rate data to calculate the rate constant at 430.0 K.

Solve

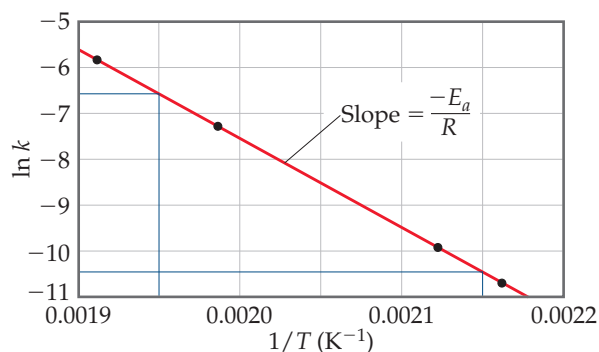
- We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$,

and the natural log of each rate constant, $\ln k$. This gives us the following table:

T (K)	$1/T$ (K ⁻¹)	$\ln k$
462.9	2.160×10^{-3}	-10.589
472.1	2.118×10^{-3}	-9.855
503.5	1.986×10^{-3}	-7.370
524.4	1.907×10^{-3}	-5.757

Continued

A graph of $\ln k$ versus $1/T$ is a straight line (Figure 14.18).



▲ Figure 14.18 Graphical determination of activation energy E_a .

The slope of the line is obtained by choosing any two well-separated points and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1} . Thus, the overall units for the slope are K. The slope equals $-E_a/R$. We use the value for the gas constant R in units of J/mol K (Table 10.2). We thus obtain

$$\begin{aligned} \text{Slope} &= -\frac{E_a}{R} \\ E_a &= -(\text{slope})(R) = -(-1.9 \times 10^4 \text{ K}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 1.6 \times 10^2 \text{ kJ/mol} = 160 \text{ kJ/mol} \end{aligned}$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.18.

- (b) To determine the rate constant, k_1 , at $T_1 = 430.0 \text{ K}$, we can use Equation 14.23 with $E_a = 160 \text{ kJ/mol}$ and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5} \text{ s}^{-1}$ and $T_2 = 462.9 \text{ K}$:

$$\ln \left(\frac{k_1}{2.52 \times 10^{-5} \text{ s}^{-1}} \right) = \left(\frac{160 \text{ kJ/mol}}{8.314 \text{ J/mol K}} \right) \left(\frac{1}{462.9 \text{ K}} - \frac{1}{430.0 \text{ K}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -3.18$$

Thus,

$$\begin{aligned} \frac{k_1}{2.52 \times 10^{-5} \text{ s}^{-1}} &= e^{-3.18} = 4.15 \times 10^{-2} \\ k_1 &= (4.15 \times 10^{-2})(2.52 \times 10^{-5} \text{ s}^{-1}) = 1.0 \times 10^{-6} \text{ s}^{-1} \end{aligned}$$

Note that the units of k_1 are the same as those of k_2 and the rate constant at 430.0 K is smaller than it is at 462.9 K , as it should be.

Practice Exercise

Using the data in Sample Exercise 14.11, which of the following is the rate constant for the rearrangement of methyl isonitrile at 320°C ?

- (a) $8.1 \times 10^{-15} \text{ s}^{-1}$ (b) $2.2 \times 10^{-13} \text{ s}^{-1}$ (c) $2.7 \times 10^{-9} \text{ s}^{-1}$
(d) $2.3 \times 10^{-1} \text{ s}^{-1}$ (e) $9.2 \times 10^3 \text{ s}^{-1}$

Self-Assessment Exercise

- 14.25 If a reaction has a rate constant of $2.0 \times 10^{-5} \text{ s}^{-1}$ at 20°C and $7.3 \times 10^{-5} \text{ s}^{-1}$ at 30°C , what is the activation energy?
(a) 280 J/mol
(b) 650 J/mol

- (c) 42 kJ/mol
(d) 96 kJ/mol

Exercises

- 14.26 (a) What factors determine whether a collision between two molecules will lead to a chemical reaction? (b) Does the rate constant for a reaction generally increase or decrease with an increase in reaction temperature? (c) Which factor is most sensitive to changes in temperature—the frequency of collisions, the orientation factor, or the fraction of molecules with energy greater than the activation energy?
- 14.27 (a) The activation energy for the reaction $\text{A(g)} \longrightarrow \text{B(g)}$ is 100 kJ/mol . Calculate the fraction of the molecule A that has an energy equal to or greater than the activation energy at 400 K . (b) Calculate this fraction for a temperature of 500 K . What is the ratio of the fraction at 500 K to that at 400 K ?
- 14.28 For the elementary process $\text{N}_2\text{O}_5(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ the activation energy (E_a) and overall ΔE are 154 kJ/mol and 136 kJ/mol , respectively. (a) Sketch the energy profile for this reaction, and label E_a and ΔE . (b) What is the activation energy for the reverse reaction?

- 14.29 Indicate whether each statement is true or false.

- (a) If you measure the rate constant for a reaction at different temperatures, you can calculate the overall enthalpy change for the reaction.
(b) Exothermic reactions are faster than endothermic reactions.
(c) If you double the temperature for a reaction, you cut the activation energy in half.

- 14.30 Data for a forward reaction is:

- (a) $E_a = 75 \text{ kJ/mol}$; $\Delta E = -20 \text{ kJ/mol}$
(b) $E_a = 100 \text{ kJ/mol}$; $\Delta E = +30 \text{ kJ/mol}$
(c) $E_a = 85 \text{ kJ/mol}$; $\Delta E = -50 \text{ kJ/mol}$

Which of these reactions will be the fastest in the reverse direction? Which will be slowest?

14.31 Understanding the high-temperature behavior of nitrogen oxides is essential for controlling pollution generated in car engines. The decomposition of nitric oxide (NO) to N_2 and O_2 is second order with a rate constant of $0.0796 \text{ M}^{-1}\text{s}^{-1}$ at 737°C and $0.0815 \text{ M}^{-1}\text{s}^{-1}$ at 947°C . Calculate the activation energy for the reaction.

14.32 The temperature dependence of the rate constant for a reaction is tabulated as follows:

Temperature (K)	$k (\text{M}^{-1} \text{s}^{-1})$
600	0.028
650	0.22
700	1.3
750	6.0
800	23

Calculate E_a and A .

14.25 (d)

Answers to Self-Assessment Exercises

14.6 | Reaction Mechanisms



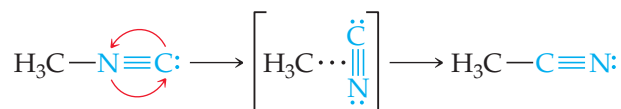
A reaction mechanism is a little like a climber of a rock face. The climber may be faced with a number of possible routes from bottom to top and it's by testing out the possibilities that the best one to accomplish the task is found.

A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those present at the end of the reaction. It provides no information, however, about the detailed steps that occur at the molecular level as the reactants are turned into products. The steps by which a reaction occurs is called the **reaction mechanism**. At the most sophisticated level, a reaction mechanism describes the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction. As we are unable to observe individual molecules as they collide and react, a reaction mechanism is always a hypothesis, however much confidence we have in our interpretation of the data. By the end of this section, you should be able to

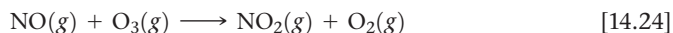
- Connect the rate law for a reaction to a mechanism given the individual steps in the mechanism.

Elementary Reactions

We have seen that reactions take place because of collisions between reacting molecules. For example, the collisions between molecules of methyl isonitrile (CH_3NC) can provide the energy to allow the CH_3NC to rearrange to acetonitrile:



Similarly, the reaction of NO and O_3 to form NO_2 and O_2 appears to occur as a result of a single collision involving suitably oriented and sufficiently energetic NO and O_3 molecules:

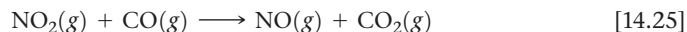


Both reactions occur in a single event or step and are called **elementary reactions**.

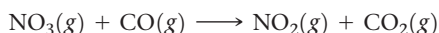
The number of molecules that participate as reactants in an elementary reaction defines the **molecularity** of the reaction. If a single molecule is involved, the reaction is **unimolecular**. The rearrangement of methyl isonitrile is a unimolecular process. Elementary reactions involving the collision of two reactant molecules are **bimolecular**. The reaction between NO and O_3 is bimolecular. Elementary reactions involving the simultaneous collision of three molecules are **termolecular**. Termolecular reactions are far less probable than unimolecular or bimolecular processes and are extremely rare. The chance that four or more molecules will collide simultaneously with any regularity is even more remote; consequently, such collisions are never proposed as part of a reaction mechanism. Thus, nearly all reaction mechanisms contain only unimolecular and bimolecular elementary reactions.

Multistep Mechanisms

The net change represented by a balanced chemical equation often occurs by a *multistep mechanism* consisting of a sequence of elementary reactions. For example, below 225°C , the reaction



appears to proceed in two elementary reactions (or two *elementary steps*), each of which is bimolecular. First, two NO_2 molecules collide, and an oxygen atom is transferred from one to the other. The resultant NO_3 then collides with a CO molecule and transfers an oxygen atom to it:



Thus, we say that the reaction occurs by a two-step mechanism.

The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.

In the present example, the sum of the two elementary reactions is

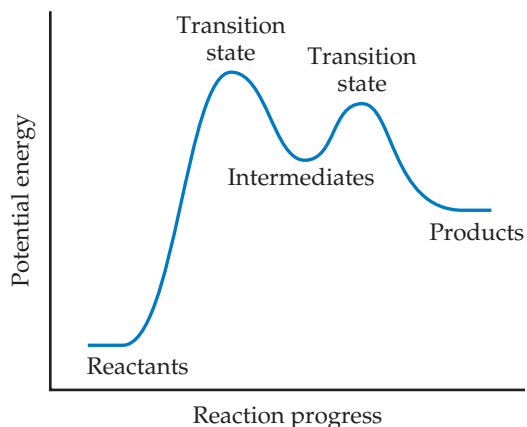


Simplifying this equation by eliminating substances that appear on both sides gives Equation 14.25, the net equation for the process.

Because NO_3 is neither a reactant nor a product of the reaction—it is formed in one elementary reaction and consumed in the next—it is called an **intermediate**. Multistep mechanisms involve one or more intermediates. Intermediates are not the same as transition states, as shown in Figure 14.19. Intermediates can be stable and can therefore sometimes be identified and even isolated. Transition states, on the other hand, are always inherently unstable and as such can never be isolated. Nevertheless, the use of advanced “ultra-fast” techniques sometimes allows us to characterize them.

Go Figure

For this profile, which elementary reaction rate is faster, intermediates converting to products or intermediates converting back to reactants?

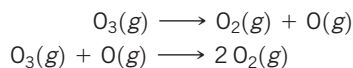


▲ **Figure 14.19** The energy profile of a reaction, showing transition states and an intermediate.

Sample Exercise 14.12

Determining Molecularity and Identifying Intermediates

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:



- Describe the molecularity of each elementary reaction in this mechanism.
- Write the equation for the overall reaction.
- Identify the intermediate(s).

SOLUTION

Analyze We are given a two-step mechanism and asked for (a) the molecularities of each of the two elementary reactions, (b) the equation for the overall process, and (c) the intermediate.

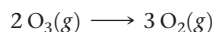
Plan The molecularity of each elementary reaction depends on the number of reactant molecules in the equation for that reaction. The overall equation is the sum of the equations for the elementary reactions. The intermediate is a substance formed in one step of the mechanism and used in another and therefore not part of the equation for the overall reaction.

Solve

- The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.
- Adding the two elementary reactions gives



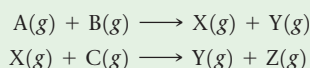
Because $O(g)$ appears in equal amounts on both sides of the equation, it can be eliminated to give the net equation for the chemical process:



- The intermediate is $O(g)$. It is neither an original reactant nor a final product but is formed in the first step of the mechanism and consumed in the second.

Practice Exercise

Consider the following two-step reaction mechanism:



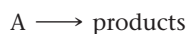
Which of the following statements about this mechanism is or are true?

- Both of the steps in this mechanism are bimolecular.
 - The overall reaction is $A(g) + B(g) + C(g) \longrightarrow Y(g) + Z(g)$.
 - The substance $X(g)$ is an intermediate in this mechanism.
- Only one of the statements is true.
 - Statements (i) and (ii) are true.
 - Statements (i) and (iii) are true.
 - Statements (ii) and (iii) are true.
 - All three statements are true.

Rate Laws for Elementary Reactions

In Section 14.3, we stressed that rate laws must be determined experimentally; they cannot be predicted from the coefficients of balanced chemical equations. We are now in a position to understand why this is so. Every reaction is made up of a series of one or more elementary steps, and the rate laws and relative speeds of these steps dictate the overall rate law for the reaction. Indeed, the rate law for a reaction can be determined from its mechanism, as we will see shortly, and compared with the experimental rate law. Thus, our next challenge in kinetics is to arrive at reaction mechanisms that lead to rate laws consistent with those observed experimentally. We start by examining the rate laws of elementary reactions.

Elementary reactions are significant in a very important way: *If a reaction is elementary, its rate law is based directly on its molecularity.* For example, consider the unimolecular reaction



As the number of A molecules increases, the number that reacts in a given time interval increases proportionally. Thus, the rate of a unimolecular process is first order:

$$\text{Rate} = k[A]$$

For bimolecular elementary steps, the rate law is second order, as in the reaction



The second-order rate law follows directly from collision theory. If we double the concentration of A, the number of collisions between the molecules of A and B doubles; likewise, if we double [B], the number of collisions between A and B doubles. Therefore, the rate law is first order in both [A] and [B] and second order overall.

The rate laws for all feasible elementary reactions are given in **Table 14.3**. Notice how each rate law follows directly from the molecularity of the reaction. It is important to remember, however, that we cannot tell by merely looking at a balanced, overall chemical equation whether the reaction involves one or several elementary steps.

The Rate-Determining Step for a Multistep Mechanism

As with the reaction in Sample Exercise 14.13, most reactions occur by mechanisms that involve two or more elementary reactions. Each step of the mechanism has its own rate constant and activation energy. Often one step is much slower than the others, and the overall rate of a reaction cannot exceed the rate of the slowest elementary step. Because

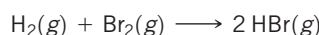
TABLE 14.3 Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

Sample Exercise 14.13

Predicting the Rate Law for an Elementary Reaction

If the following reaction occurs in a single elementary reaction, predict its rate law:



SOLUTION

Analyze We are given the equation and asked for its rate law, assuming that it is an elementary process.

Plan Because we are assuming that the reaction occurs as a single elementary reaction, we are able to write the rate law using the coefficients for the reactants in the equation as the reaction orders.

Solve The reaction is bimolecular, involving one molecule of H_2 and one molecule of Br_2 . Thus, the rate law is first order in each reactant and second order overall:

$$\text{Rate} = k[\text{H}_2][\text{Br}_2]$$

Comment Experimental studies of this reaction show that the reaction actually has a very different rate law:

$$\text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$$

Because the experimental rate law differs from the one obtained by assuming a single elementary reaction, we can conclude that the mechanism cannot occur by a single elementary step. It must, therefore, involve two or more elementary steps.

Practice Exercise

Consider the following reaction: $2 \text{A} + \text{B} \longrightarrow \text{X} + 2 \text{Y}$. You are told that the first step in the mechanism of this reaction has the following rate law: $\text{Rate} = k[\text{A}][\text{B}]$. Which of the following could be the first step in the reaction mechanism (note that substance Z is an intermediate)?

- (a) $\text{A} + \text{A} \longrightarrow \text{Y} + \text{Z}$
- (b) $\text{A} \longrightarrow \text{X} + \text{Z}$
- (c) $\text{A} + \text{A} + \text{B} \longrightarrow \text{X} + \text{Y} + \text{Y}$
- (d) $\text{B} \longrightarrow \text{X} + \text{Y}$
- (e) $\text{A} + \text{B} \longrightarrow \text{X} + \text{Z}$

the slow step limits the overall reaction rate, it is called the **rate-determining step** (or *rate-limiting step*).

To understand the concept of the rate-determining step for a reaction, consider a toll road with two toll plazas (Figure 14.20). Cars enter the toll road at point 1 and pass through toll plaza A. They then pass an intermediate point 2 before passing through toll plaza B and arriving at point 3. We can envision this trip along the toll road as occurring in two elementary steps:

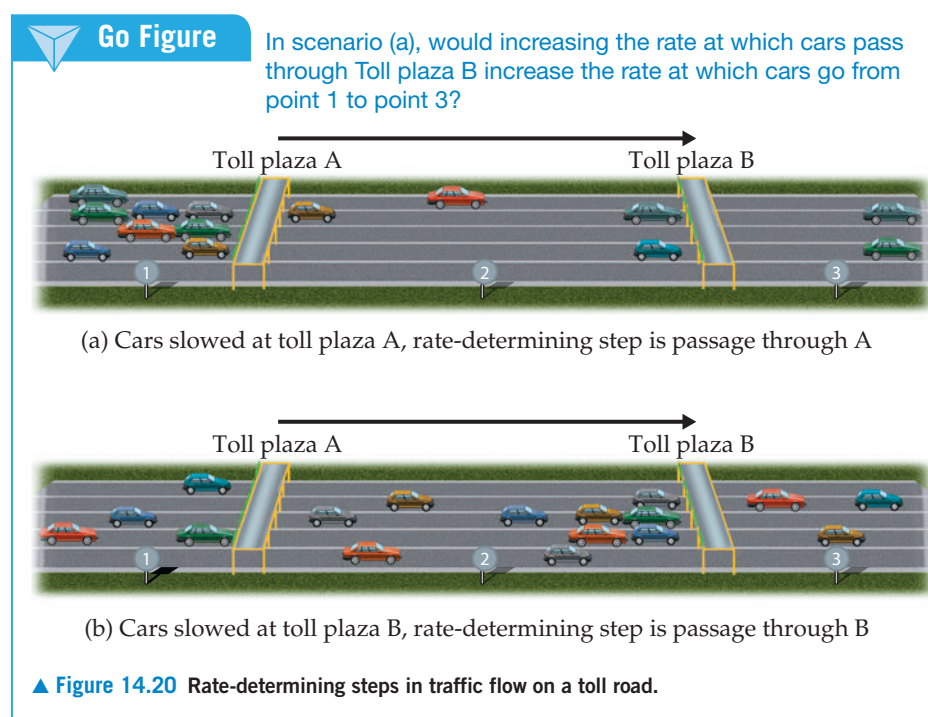
Step 1:	Point 1 $\longrightarrow$ Point 2	(through toll plaza A)
Step 2:	Point 2 $\longrightarrow$ Point 3	(through toll plaza B)
Overall:	Point 1 $\longrightarrow$ Point 3	(through both toll plazas)

Now suppose that one or more gates at toll plaza A are malfunctioning, so that traffic backs up behind the gates, as depicted in Figure 14.20(a). The rate at which cars can get to point 3 is limited by the rate at which they can get through the traffic jam at plaza A. Thus, step 1 is the rate-determining step of the journey along the toll road. If, however, all gates at A are functioning but one or more at B are not, traffic flows quickly through A but gets backed up at B, as depicted in Figure 14.20(b). In this case, step 2 is the rate-determining step.

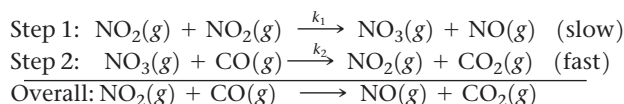
In the same way, *the slowest step in a multistep reaction determines the overall rate*. By analogy to Figure 14.20(a), the rate of a fast step following the rate-determining step does not speed up the overall rate. If the slow step is not the first one, as is the case in Figure 14.20(b), the faster preceding steps produce intermediate products that accumulate before being consumed in the slow step. In either case, *the rate-determining step governs the rate law for the overall reaction*.

Mechanisms with a Slow Initial Step

We can most easily see the relationship between the slow step in a mechanism and the rate law for the overall reaction by considering an example in which the first step in a multistep mechanism is the rate-determining step. Consider the reaction of NO_2 and CO to produce NO and CO_2 (Equation 14.25). Below 225°C , it is found experimentally that the rate law for this reaction is second order in NO_2 and zero order in CO : $\text{Rate} = k[\text{NO}_2]^2$.



Can we propose a reaction mechanism consistent with this rate law? Consider the two-step mechanism:*



Step 2 is much faster than step 1; that is, $k_2 \gg k_1$, telling us that the intermediate $\text{NO}_3(\text{g})$ is slowly produced in step 1 and immediately consumed in step 2.

Because step 1 is slow and step 2 is fast, step 1 is the rate-determining step. Thus, the rate of the overall reaction depends on the rate of step 1, and the rate law of the overall reaction equals the rate law of step 1. Step 1 is a bimolecular process that has the rate law

$$\text{Rate} = k_1[\text{NO}_2]^2$$

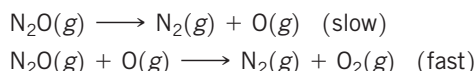
Thus, the rate law predicted by this mechanism agrees with the one observed experimentally. The reactant CO is absent from the rate law because it reacts in a step that follows the rate-determining step.

A scientist would not, at this point, say that we have “proved” that this mechanism is correct. All we can say is that the rate law predicted by the mechanism is *consistent with experiment*. We can often envision a different sequence of steps that leads to the same rate law. If, however, the predicted rate law of the proposed mechanism disagrees with experiment, we know for certain that the mechanism cannot be correct.

Sample Exercise 14.14

Determining the Rate Law for a Multistep Mechanism

The decomposition of nitrous oxide, N_2O , is believed to occur by a two-step mechanism:



(a) Write the equation for the overall reaction. (b) Write the rate law for the overall reaction.

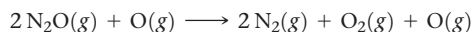
SOLUTION

Analyze Given a multistep mechanism with the relative speeds of the steps, we are asked to write the overall reaction and the rate law for that overall reaction.

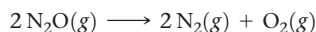
Plan (a) Find the overall reaction by adding the elementary steps and eliminating the intermediates. (b) The rate law for the overall reaction will be that of the slow, rate-determining step.

Solve

(a) Adding the two elementary reactions gives



Omitting the intermediate, $\text{O}(\text{g})$, which occurs on both sides of the equation, gives the overall reaction:



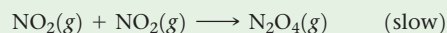
(b) The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

$$\text{Rate} = k[\text{N}_2\text{O}]$$

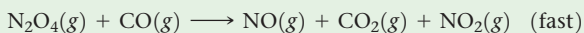
Practice Exercise

An alternative two-step reaction mechanism has been proposed for the reaction $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$, which was discussed on page 692:

Step 1:



Step 2:



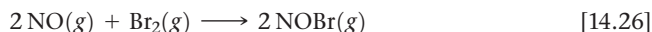
Which experiment would allow you to distinguish between the two proposed mechanisms?

(a) Run trials with different initial concentrations of $\text{NO}_2(\text{g})$ and measure the initial reaction rates. (b) Run trials with different initial concentrations of $\text{CO}(\text{g})$ and measure the initial reaction rates. (c) Conduct experiments to identify the reaction intermediate(s). (d) It is not possible to distinguish between the two proposed reaction mechanisms.

*Note the rate constants k_1 and k_2 written above the reaction arrows. The subscript on each rate constant identifies the elementary step involved. Thus, k_1 is the rate constant for step 1, and k_2 is the rate constant for step 2. A negative subscript refers to the rate constant for the reverse of an elementary step. For example, k_{-1} is the rate constant for the reverse of the first step.

Mechanisms with a Fast Initial Step

It is possible, but not particularly straightforward, to derive the rate law for a mechanism in which an intermediate is a reactant in the rate-determining step. This situation arises in multistep mechanisms when the first step is fast and therefore *not* the rate-determining step. Let's consider one example: the gas-phase reaction of nitric oxide (NO) with bromine (Br_2):



The experimentally determined rate law for this reaction is second order in NO and first order in Br_2 :

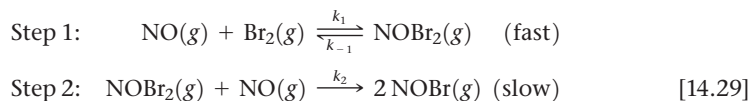
$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2] \quad [14.27]$$

We seek a reaction mechanism that is consistent with this rate law. One possibility is that the reaction occurs in a single termolecular step:



As noted in Practice Exercise 2 of Exercise 14.13, this does not seem likely because termolecular processes are so rare.

Let's consider an alternative mechanism that does not involve a termolecular step:



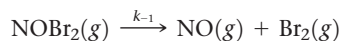
In this mechanism, step 1 involves two processes: a forward reaction and its reverse.

Because step 2 is the rate-determining step, the rate law for that step governs the rate of the overall reaction:

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}] \quad [14.30]$$

Note that NOBr_2 is an intermediate generated in the forward reaction of step 1. Intermediates are usually unstable and have a low, unknown concentration. Thus, the rate law of Equation 14.30 depends on the unknown concentration of an intermediate, which isn't desirable. We want instead to express the rate law for a reaction in terms of the reactants, or the products if necessary, of the reaction.

With the aid of some assumptions, we can express the concentration of the intermediate NOBr_2 in terms of the concentrations of the starting reactants NO and Br_2 . We first assume that NOBr_2 is unstable and does not accumulate to any significant extent in the reaction mixture. Once formed, NOBr_2 can be consumed either by reacting with NO to form NOBr or by falling back apart into NO and Br_2 . The first of these possibilities is step 2 of our alternative mechanism, a slow process. The second is the reverse of step 1, a unimolecular process:



Because step 2 is slow, we assume that most of the NOBr_2 falls apart according to this reaction. Thus, we have both the forward and reverse reactions of step 1 occurring much faster than step 2. Because they occur rapidly relative to step 2, the forward and reverse reactions of step 1 establish an equilibrium. As in any other dynamic equilibrium, the rate of the forward reaction equals that of the reverse reaction:

$$\begin{array}{ccc} k[\text{NO}][\text{Br}_2] & = & k_{-1}[\text{NOBr}_2] \\ \text{Rate of forward reaction} & & \text{Rate of reverse reaction} \end{array}$$

Solving for $[\text{NOBr}_2]$, we have

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]$$

Substituting this relationship into Equation 14.30, we have

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2][\text{NO}] = k[\text{NO}]^2[\text{Br}_2]$$

where the experimental rate constant k equals k_2k_1/k_{-1} . This expression is consistent with the experimental rate law (Equation 14.27). Thus, our alternative mechanism (Equation 14.29), which involves two steps but only unimolecular and bimolecular processes, is far more probable than the single-step termolecular mechanism of Equation 14.28.

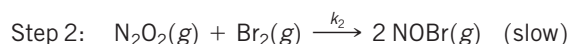
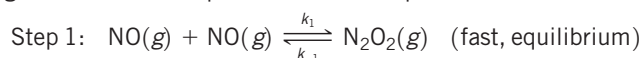
In general, whenever a fast step precedes a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the fast step.

So far we have considered only three reaction mechanisms: one for a reaction that occurs in a single elementary step and two for simple multistep reactions where there is one rate-determining step. There are other more complex mechanisms, however. If you take a biochemistry class, for example, you will learn about cases in which the concentration of an intermediate cannot be neglected in deriving the rate law. Furthermore, some mechanisms require a large number of steps, sometimes 35 or more, to arrive at a rate law that agrees with experimental data!

Sample Exercise 14.15

Deriving the Rate Law for a Mechanism with a Fast Initial Step

Show that the following mechanism for Equation 14.26 also produces a rate law consistent with the experimentally observed one:



SOLUTION

Analyze We are given a mechanism with a fast initial step and asked to write the rate law for the overall reaction.

Plan The rate law of the slow elementary step in a mechanism determines the rate law for the overall reaction. Thus, we first write the rate law based on the molecularity of the slow step. In this case, the slow step involves the intermediate N_2O_2 as a reactant. Experimental rate laws, however, do not contain the concentrations of intermediates; instead they are expressed in terms of the concentrations of reactants, and in some cases products. Thus, we must relate the concentration of N_2O_2 to the concentration of NO by assuming that an equilibrium is established in the first step.

Solve The second step is rate determining, so the overall rate is

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{Br}_2]$$

We solve for the concentration of the intermediate N_2O_2 by assuming that an equilibrium is established in step 1; thus, the rates of the forward and reverse reactions in step 1 are equal:

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Solving for the concentration of the intermediate, N_2O_2 , gives

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

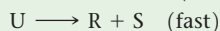
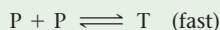
Substituting this expression into the rate expression gives

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}} [\text{NO}]^2 [\text{Br}_2] = k [\text{NO}]^2 [\text{Br}_2]$$

Thus, this mechanism also yields a rate law consistent with the experimental one. Remember: There may be more than one mechanism that leads to an observed experimental rate law!

Practice Exercise

Consider the following hypothetical reaction:
 $2 \text{P} + \text{Q} \longrightarrow 2 \text{R} + \text{S}$. The following mechanism is proposed for this reaction:



Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?

- (a) $\text{Rate} = k[\text{P}]^2$ (b) $\text{Rate} = k[\text{P}][\text{Q}]$ (c) $\text{Rate} = k[\text{P}]^2[\text{Q}]$
 (d) $\text{Rate} = k[\text{P}][\text{Q}]^2$ (e) $\text{Rate} = k[\text{U}]$

Self-Assessment Exercise

14.33 For the reaction: $2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g)$ a two-step mechanism was proposed with Step 1 as the rate-determining step:



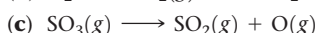
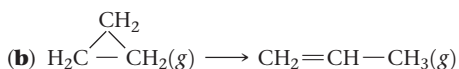
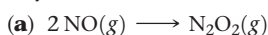
What rate law is consistent with this mechanism?

- (a) $\text{Rate} = k[\text{NO}_2][\text{F}_2]$
 (b) $\text{Rate} = k[\text{NO}_2][\text{F}]$
 (c) $\text{Rate} = k[\text{NO}_2]^2[\text{F}_2]$

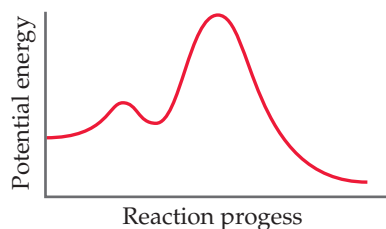
Exercises

14.34 (a) Can an intermediate appear as a reactant in the first step of a reaction mechanism? (b) On a reaction energy profile diagram, is an intermediate represented as a peak or a valley? (c) If a molecule like Cl_2 falls apart in an elementary reaction, what is the molecularity of the reaction?

14.35 What is the molecularity of each of the following elementary reactions? Write the rate law for each.

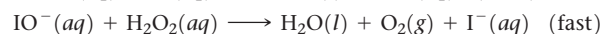
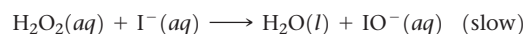


14.36 Consider the following energy profile.



(a) How many elementary reactions are in the reaction mechanism? (b) How many intermediates are formed in the reaction? (c) Which step is rate limiting? (d) For the overall reaction, is ΔE positive, negative, or zero?

14.37 The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:

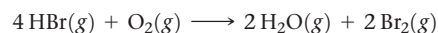


(a) Write the chemical equation for the overall process.

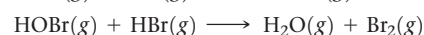
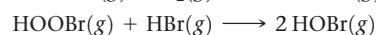
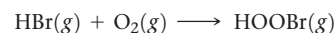
(b) Identify the intermediate, if any, in the mechanism.

(c) Assuming that the first step of the mechanism is rate determining, predict the rate law for the overall process.

14.38 You have studied the gas-phase oxidation of HBr by O_2 :



You find the reaction to be first order with respect to HBr and first order with respect to O_2 . You propose the following mechanism:



(a) Confirm that the elementary reactions add to give the overall reaction. (b) Based on the experimentally determined rate law, which step is rate determining? (c) What are the intermediates in this mechanism? (d) If you are unable to detect HOBr or HOOBr among the products, does this disprove your mechanism?

14.33 (a)

Answers to Self-Assessment Exercises

14.7 | Catalysis



We have seen that the rate of a reaction is very dependent on the fraction of reacting molecules that have above a minimum amount of energy, the activation energy, and the rate increases rapidly as the temperature of the reaction increases. This allows us to perform quite slow reactions simply by heating them. But what about a situation wherein

we cannot change the temperature? A healthy person maintains a body temperature of $37 \pm 0.5^\circ\text{C}$, yet there is a myriad of very different chemical reactions that would be vanishingly slow under normal laboratory conditions at that temperature. The body employs a vast number of catalysts to facilitate these reactions while maintaining a constant temperature of 37°C . Occasionally a person may not produce sufficient amount of a catalyst and supplementation may be needed; for example a diabetic may require insulin injections in order to metabolize blood sugars.

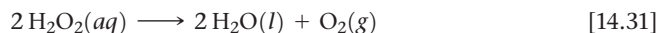
By the end of this section, you should be able to

- Explain the principles underlying catalysis.

A **catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself. Most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts. Much industrial chemical research is devoted to the search for more effective catalysts for reactions of commercial importance. Extensive research efforts also are devoted to finding means of inhibiting or removing certain catalysts that promote undesirable reactions, such as those that corrode metals, age our bodies, and cause tooth decay.

Homogeneous Catalysis

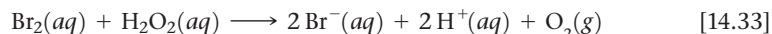
A catalyst that is present in the same phase as the reactants in a reaction mixture is called a **homogeneous catalyst**. Examples abound both in solution and in the gas phase. Consider, for example, the decomposition of aqueous hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, into water and oxygen:



In the absence of a catalyst, this reaction occurs extremely slowly. Many substances are capable of catalyzing the reaction, however, including bromide ion, which reacts with hydrogen peroxide in acidic solution, forming aqueous bromine and water (Figure 14.21).



If this were the complete reaction, bromide ion would not be a catalyst because it undergoes chemical change during the reaction. However, hydrogen peroxide also reacts with the $\text{Br}_2(\text{aq})$ generated in Equation 14.32:



The sum of Equations 14.32 and 14.33 is just Equation 14.31, a result that you can check for yourself.

When the H_2O_2 has been completely decomposed, we are left with a colorless solution of $\text{Br}^-(\text{aq})$, which means that this ion is indeed a catalyst of the reaction because it speeds up the reaction without itself undergoing any net change. In contrast, Br_2 is an intermediate because it is first formed (Equation 14.32) and then consumed (Equation 14.33). The color change we see in Figure 14.22 illustrates that the presence of intermediates can in some cases be readily detected. Neither the catalyst nor the intermediate appears in the equation for the overall reaction. Notice, however, that *the catalyst is present at the start of the reaction, whereas the intermediate is formed during the course of the reaction.*

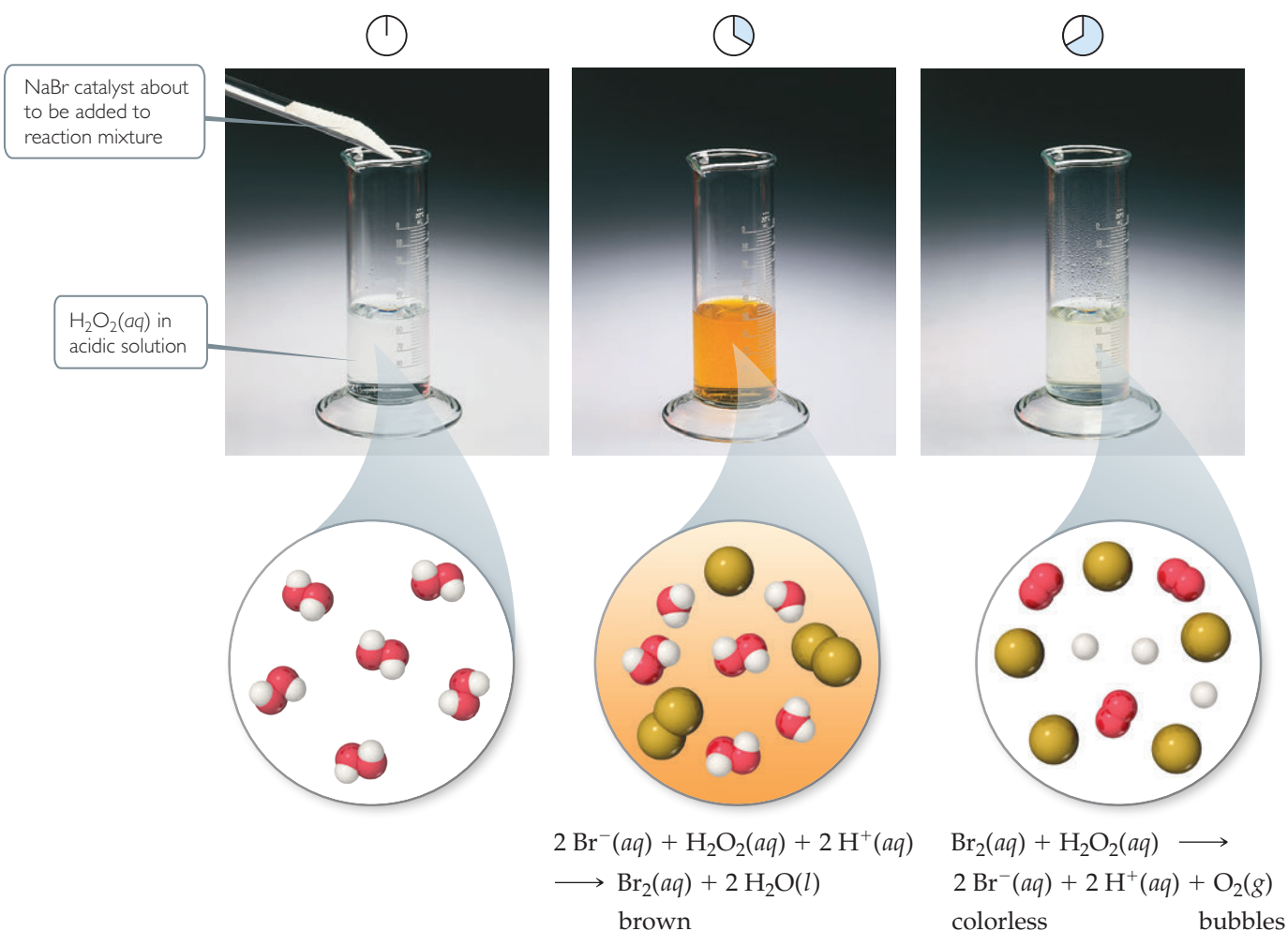
How does a catalyst work? If we think about the general form of rate laws (Equation 14.7, $\text{rate} = k[\text{A}]^m[\text{B}]^n$), we conclude that the catalyst must affect the numerical value of k , the rate constant. On the basis of the Arrhenius equation (Equation 14.21, $k = Ae^{-E_a/RT}$), k is determined by the activation energy (E_a) and the frequency factor (A). A catalyst may affect the rate of reaction by altering the value of either E_a or A . We can envision this happening in two ways: The catalyst could provide a new mechanism for the reaction that has an E_a value lower than the E_a value for the uncatalyzed reaction, or the catalyst could assist in the orientation of reactants and so increase A . The most dramatic catalytic effects come from lowering E_a . As a general rule, *a catalyst provides a different mechanism for the chemical reaction of lower overall activation energy.*

In the decomposition of hydrogen peroxide, for example, two successive reactions of H_2O_2 , first with bromide and then with bromine, take place. Because these two reactions



Go Figure

Which species is responsible for the brownish color in the middle cylinder: H_2O_2 , Br_2 , Na^+ , Br^- , or O_2 ? Is the brown substance a catalyst or an intermediate?



▲ **Figure 14.21 Homogeneous catalysis.** Effect of catalyst on the speed of hydrogen peroxide decomposition to water and oxygen gas.

together serve as a catalytic pathway for hydrogen peroxide decomposition, *both* of them must have significantly lower activation energies than the uncatalyzed decomposition (**Figure 14.22**).

Heterogeneous Catalysis

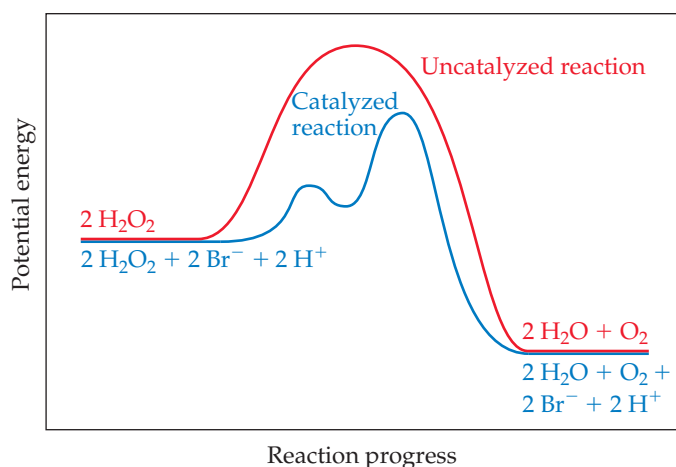
A **heterogeneous catalyst** is one that exists in a phase different from the phase of the reactant molecules, usually as a solid in contact with either gaseous reactants or reactants in a liquid solution. Many industrially important reactions are catalyzed by the surfaces of solids. For example, raw petroleum is transformed into smaller hydrocarbon molecules by using what are called “cracking” catalysts. Heterogeneous catalysts are often composed of metals or metal oxides.

The initial step in heterogeneous catalysis is usually **adsorption** of reactants. (Adsorption refers to the binding of molecules to a surface, whereas absorption refers to the uptake of molecules into the interior of a substance.) Adsorption occurs because the atoms or ions at the surface of a solid are extremely reactive. Because the catalyzed reaction occurs on the surface, special methods are often used to prepare catalysts so that they have very large surface areas. Unlike their counterparts in the interior of the substance, surface atoms and ions have unused bonding capacity that can be used to bond molecules from the gas or solution phase to the surface of the solid.



Go Figure

How many steps are there in the catalyzed reaction?



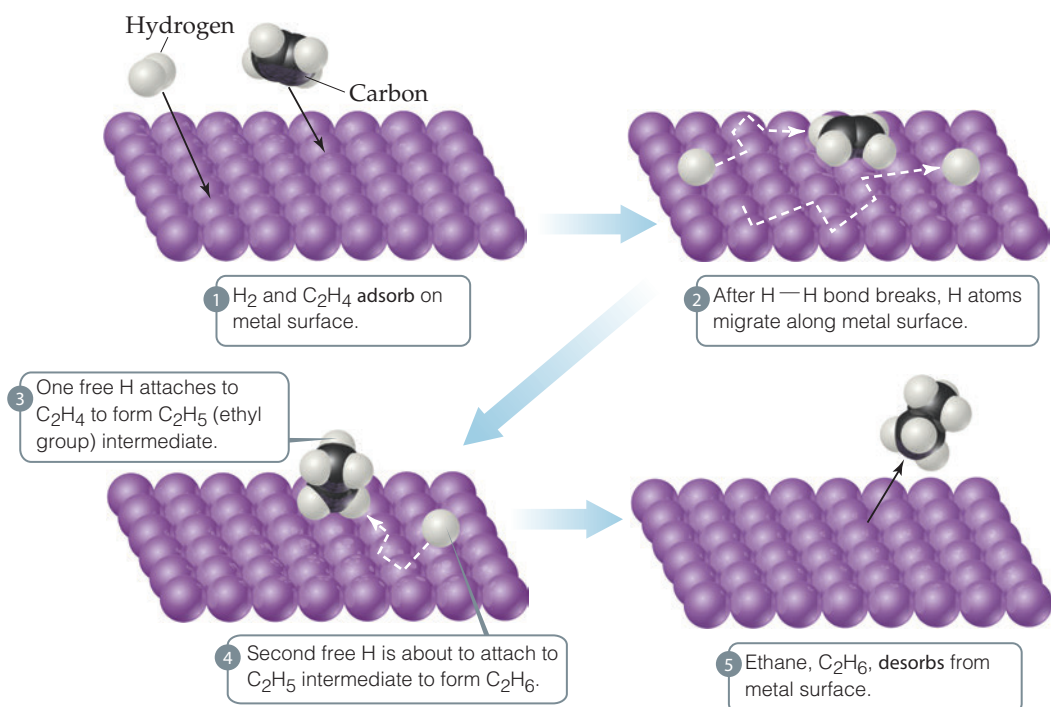
▲ **Figure 14.22** Energy profiles for the uncatalyzed and bromide-catalyzed decomposition of H_2O_2 .

The reaction of hydrogen gas with ethene gas to form ethane gas provides an example of heterogeneous catalysis:



Even though this reaction is exothermic, it occurs very slowly in the absence of a catalyst. In the presence of a finely powdered metal, however, such as nickel, palladium, or platinum, the reaction occurs easily at room temperature via the mechanism diagrammed in **Figure 14.23**. Both ethene and hydrogen are adsorbed on the metal surface. Upon adsorption, the $\text{H}-\text{H}$ bond of H_2 breaks, leaving two H atoms initially bonded to the metal surface but relatively free to move. When a hydrogen encounters an adsorbed ethene molecule, it can form a σ bond to one of the carbon atoms, effectively destroying the $\text{C}-\text{C}$ π bond and leaving an *ethyl group* (C_2H_5) bonded to the surface via a metal-to-carbon σ bond. This σ bond is relatively weak, so when the other carbon atom also encounters a hydrogen atom, a sixth $\text{C}-\text{H}$ σ bond is readily formed, and an ethane molecule (C_2H_6) is released from the metal surface.

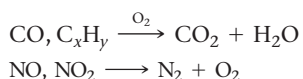
► **Figure 14.23** Heterogeneous catalysis. Mechanism for reaction of ethene with hydrogen on a catalytic surface.



CHEMISTRY PUT TO WORK Catalytic Converters

Heterogeneous catalysis plays a major role in the fight against urban air pollution. Two components of automobile exhausts that help form photochemical smog are nitrogen oxides and unburned hydrocarbons. In addition, automobile exhaust may contain considerable quantities of carbon monoxide. Even with the most careful attention to engine design, it is impossible under normal driving conditions to reduce the quantity of these pollutants to an acceptable level in the exhaust gases. It is therefore necessary to remove them from the exhaust before they are vented to the air. This removal is accomplished in the *catalytic converter*.

The catalytic converter, which is part of an automobile's exhaust system, must perform two functions: (1) oxidation of CO and unburned hydrocarbons (C_xH_y) to carbon dioxide and water, and (2) reduction of nitrogen oxides to nitrogen gas:



These two functions require different catalysts, so the development of a successful catalyst system is a difficult challenge. The catalysts must be effective over a wide range of operating temperatures. They must continue to be active despite the fact that various components of the exhaust can block the active sites of the catalyst. And the catalysts must be sufficiently rugged to withstand exhaust gas turbulence and the mechanical shocks of driving under various conditions for thousands of miles.

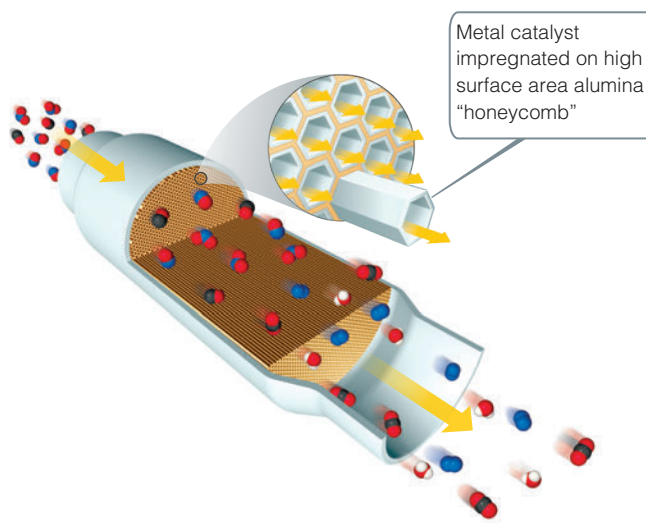
Catalysts that promote the combustion of CO and hydrocarbons are, in general, the transition-metal oxides and the noble metals. These materials are supported on a structure (Figure 14.24) that allows the best possible contact between the flowing exhaust gas and the catalyst surface. A honeycomb structure made from alumina (Al_2O_3) and impregnated with the catalyst that is employed. Such catalysts operate by first adsorbing oxygen gas present in the exhaust gas. This adsorption weakens the O—O bond in O_2 , so that oxygen atoms are available for reaction with adsorbed CO to form CO_2 . Hydrocarbon oxidation probably proceeds somewhat similarly, with the hydrocarbons first being adsorbed followed by rupture of a C—H bond.

Transition-metal oxides and noble metals are also the most effective catalysts for reduction of NO to N_2 and O_2 . The catalysts that are most effective in one reaction, however, are usually much less effective in the other. It is therefore necessary to have two catalytic components.

Catalytic converters contain remarkably efficient heterogeneous catalysts. The automotive exhaust gases are in contact with the catalyst for only 100 to 400 ms, but in this very short time, 96% of the hydrocarbons and CO is converted to CO_2 and H_2O , and the emission of nitrogen oxides is reduced by 76%.

Although the exact combination of catalysts used varies from one catalytic converter to another, precious metals are an essential component of any catalytic converter. Platinum is very good at catalyzing the oxidation reactions and has good resistance to impurities such as lead, sulfur, and phosphorus that can poison or disable the catalyst. Palladium is a slightly less expensive alternative to platinum, but it is more sensitive to poisoning from impurities in the exhaust stream. Rhodium is the metal of choice for reduction of nitrogen oxides and has reasonable activity for the oxidation reactions. Unfortunately, it is even rarer and more expensive than platinum. Catalytic converters currently account for approximately 35% of the world's use of platinum, 65% of palladium, and 95% of rhodium. Deposits of these metals tend to be concentrated in South Africa and Russia.

Related Exercises: 14.31, 14.95, 14.43, 14.133



▲ Figure 14.24 Cross section of a catalytic converter.

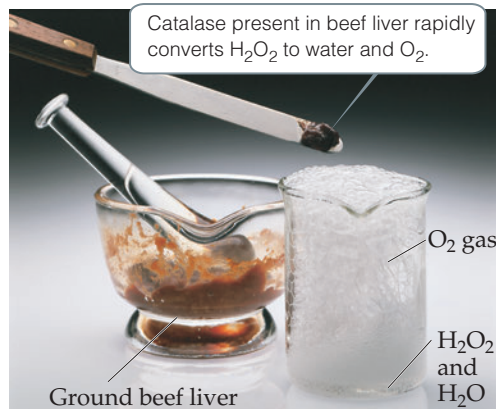
Enzymes

The human body is characterized by an extremely complex system of interrelated chemical reactions, all of which must occur at carefully controlled rates to maintain life. A large number of marvelously efficient biological catalysts known as **enzymes** are necessary for many of these reactions to occur at suitable rates. Most enzymes are large protein molecules with molecular weights ranging from about 10,000 to about 1 million u. They are very selective in the reactions they catalyze, and some are absolutely specific, operating for only one substance in only one reaction. The decomposition of hydrogen peroxide, for example, is an important biological process. Because hydrogen peroxide is strongly oxidizing, it can be physiologically harmful. For this reason, the blood and liver of mammals contain an enzyme, *catalase*, that catalyzes the decomposition of hydrogen peroxide into water and oxygen (Equation 14.31). Figure 14.25 shows the dramatic acceleration of this chemical reaction by the catalase in beef liver.

The reaction any given enzyme catalyzes takes place at a specific location in the enzyme called the **active site**. The substances that react at this site are called **substrates**. The **lock-and-key model** provides a simple explanation

Go Figure

Why is the reaction faster when the liver is ground up?



▲ Figure 14.25 Enzymes speed up reactions.

for the specificity of an enzyme (Figure 14.26). The substrate is pictured as fitting neatly into the active site, much like a key fits into a lock.

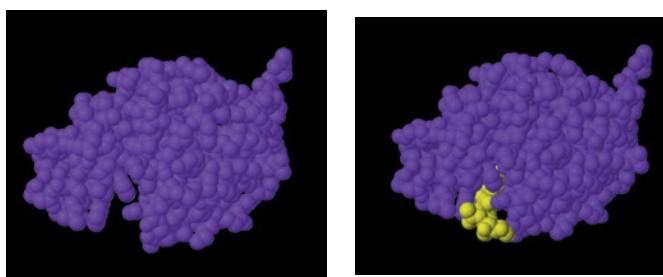
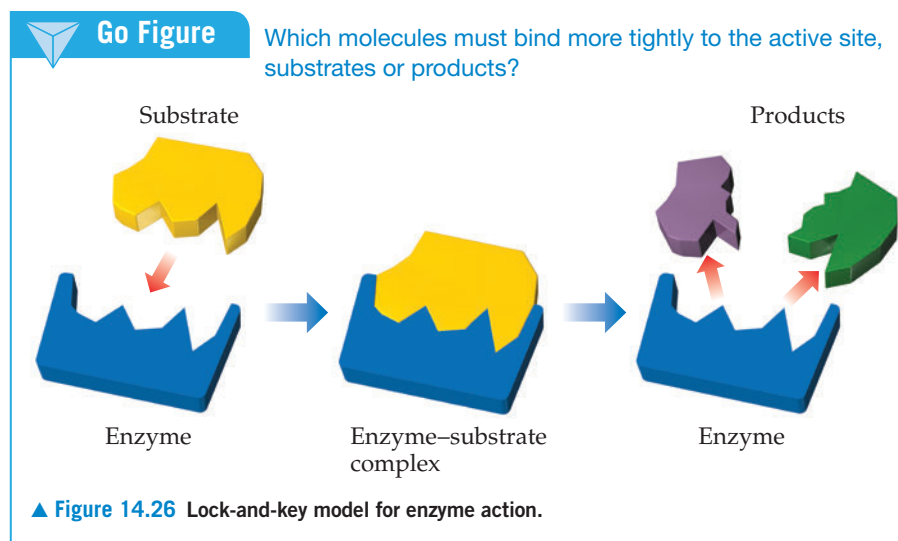
Lysozyme is an enzyme that is important to the functioning of our immune system because it accelerates reactions that damage (or “lyse”) bacterial cell walls. Figure 14.27 shows a model of the enzyme lysozyme without and with a bound substrate molecule.

The combination of enzyme and substrate is called the *enzyme–substrate complex*. Although Figure 14.26 shows both the active site and its substrate as having a fixed shape, the active site is often fairly flexible and so may change shape as it binds the substrate. The binding between substrate and active site involves dipole–dipole attractions, hydrogen bonds, and dispersion forces.

As substrate molecules enter the active site, they are somehow activated so that they are capable of reacting rapidly. This activation process may occur, for example, by the withdrawal or donation of electron density from a particular bond or group of atoms in the enzyme’s active site. In addition, the substrate may become distorted in the process of fitting into the active site and made more reactive. Once the reaction occurs, the products depart from the active site, allowing another substrate molecule to enter.

The activity of an enzyme is destroyed if some molecule other than the substrate specific to that enzyme binds to the active site and blocks entry of the substrate. Such substances are called *enzyme inhibitors*. Nerve poisons and certain toxic metal ions, such as lead and mercury, are believed to act in this way to inhibit enzyme activity. Some other poisons act by attaching elsewhere on the enzyme, thereby distorting the active site so that the substrate no longer fits.

Enzymes are enormously more efficient than nonbiochemical catalysts. The number of individual catalyzed reaction events occurring at a particular active site, called the *turn-over number*, is generally in the range of 10^3 to 10^7 per second. Such large turnover numbers correspond to very low activation energies. Compared with a simple chemical catalyst, enzymes can increase the rate constant for a given reaction by a millionfold or more.



▲ **Figure 14.27** Lysozyme was one of the first enzymes for which a structure–function relationship was described. This model shows how the substrate (yellow) “fits” into the active site of the enzyme.

CHEMISTRY AND LIFE Nitrogen Fixation and Nitrogenase

Nitrogen is one of the most essential elements in living organisms, found in many compounds vital to life, including proteins, nucleic acids, vitamins, and hormones. Nitrogen is continually cycling through the biosphere in various forms, as shown in **Figure 14.28**. For example, certain microorganisms convert the nitrogen in animal waste and dead plants and animals into $\text{N}_2(\text{g})$, which then returns to the atmosphere. For the food chain to be sustained, there must be a means of converting atmospheric $\text{N}_2(\text{g})$ into a form plants can use.

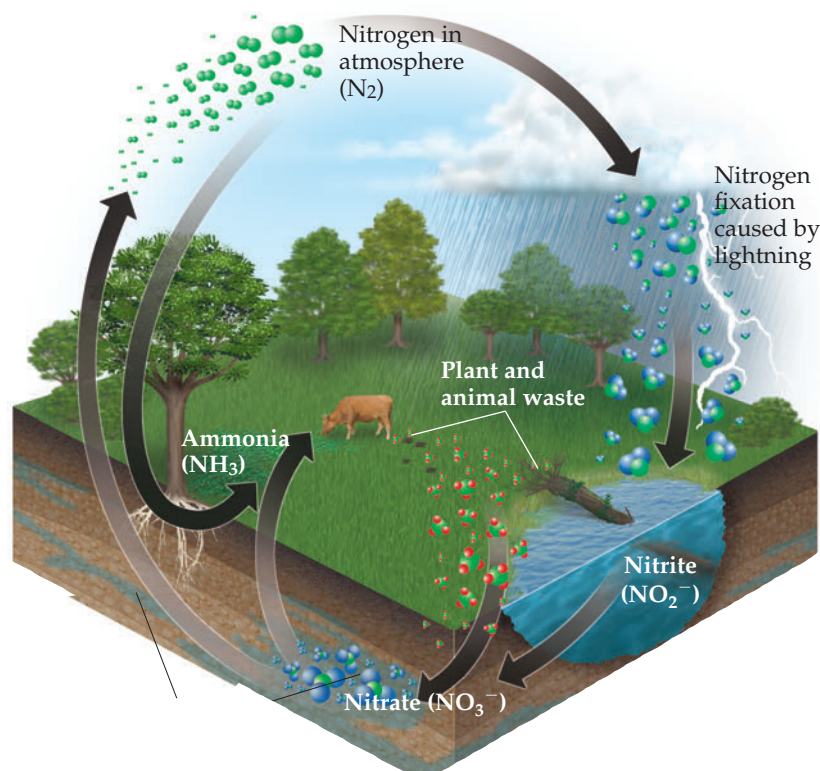
For this reason, if a chemist were asked to name the most important chemical reaction in the world, she might easily say *nitrogen fixation*, the process by which atmospheric $\text{N}_2(\text{g})$ is converted into compounds suitable for plant use. Some fixed nitrogen results from the action of lightning on the atmosphere, and some is produced industrially using a process we will discuss in Chapter 15. About 60% of fixed nitrogen, however, is a consequence of the action of the remarkable and complex enzyme *nitrogenase*. This enzyme is *not* present in humans or other animals; rather, it is found in bacteria that live in the root nodules of certain plants, such as the legumes clover and alfalfa.

Nitrogenase converts N_2 into NH_3 , a process that, in the absence of a catalyst, has a very large activation energy. This process is a *reduction* reaction in which the oxidation state of N is reduced from 0 in N_2 to -3 in NH_3 . The mechanism by which nitrogenase reduces N_2 is not fully understood. Like many other enzymes, including catalase, the active site of nitrogenase contains transition-metal atoms; such enzymes are called *metalloenzymes*. Because transition metals can readily change oxidation state, metalloenzymes are especially useful for effecting transformations in which substrates are either oxidized or reduced.

It has been known for nearly 40 years that a portion of nitrogenase contains iron and molybdenum atoms. This portion, called the *FeMo-cofactor*, is thought to serve as the active site of the enzyme. The FeMo-cofactor of nitrogenase is a cluster of seven Fe atoms and one Mo atom, all linked by sulfur atoms (**Figure 14.29**).

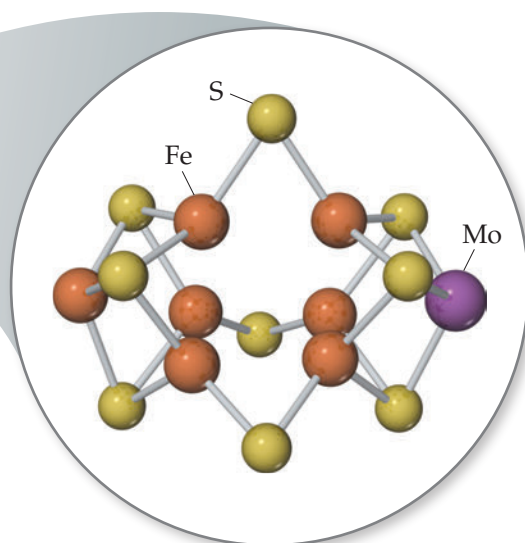
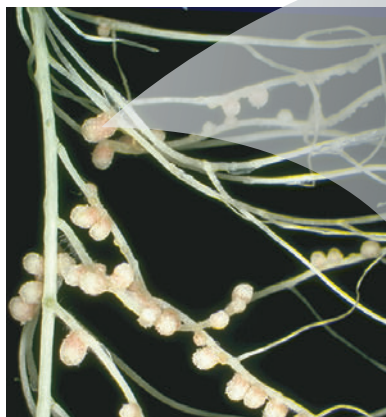
It is one of the wonders of life that simple bacteria can contain beautifully complex and vitally important enzymes such as nitrogenase. Because of this enzyme, nitrogen is continually cycled between its comparatively inert role in the atmosphere and its critical role in living organisms. Without nitrogenase, life as we know it could not exist on Earth.

Related Exercises: 14.45, 14.124, 14.125



▲ **Figure 14.28** Simplified picture of the nitrogen cycle.

► **Figure 14.29** The FeMo-cofactor of nitrogenase. Nitrogenase is found in nodules in the roots of certain plants, such as the white clover roots shown at the left. The cofactor, which is thought to be the active site of the enzyme, contains seven Fe atoms and one Mo atom, linked by sulfur atoms. The molecules on the outside of the cofactor connect it to the rest of the protein.



Self-Assessment Exercise

14.39 True or false: catalysts increase the yield of a reaction.

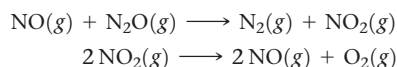
- (a) True
(b) False

Exercises

14.40 (a) Most commercial heterogeneous catalysts are extremely finely divided solid materials. Why is particle size important? (b) What role does adsorption play in the action of a heterogeneous catalyst?

14.41 In solution, chemical species as simple as H^+ and OH^- can serve as catalysts for reactions. Imagine you could measure the $[\text{H}^+]$ of a solution containing an acid-catalyzed reaction as it occurs. Assume the reactants and products themselves are neither acids nor bases. Sketch the $[\text{H}^+]$ concentration profile you would measure as a function of time for the reaction, assuming $t = 0$ is when you add a drop of acid to the reaction.

14.42 The addition of NO accelerates the decomposition of N_2O , possibly by the following mechanism:



(a) What is the chemical equation for the overall reaction? Show how the two steps can be added to give the overall equation. (b) Is NO serving as a catalyst or an intermediate in this reaction? (c) If experiments show that during the decomposition of N_2O , NO_2 does not accumulate in measurable quantities, does this rule out the proposed mechanism?

14.43 (a) If you were going to build a system to check the effectiveness of catalytic converters on cars, what substances would you want to look for in the car exhaust? (b) Car catalytic converters have to work at high temperatures, as hot exhaust gases stream through them. In what ways could

this be an advantage? In what ways a disadvantage? (c) Why is the rate of flow of exhaust gases over a catalytic converter important?

14.44 Heterogeneous catalysts that perform hydrogenation reactions, as illustrated in Figure 14.23, are subject to “poisoning,” which shuts down their catalytic ability. Compounds of sulfur are often poisons. Suggest a mechanism by which such compounds might act as poisons.

14.45 The enzyme urease catalyzes the reaction of urea, $(\text{NH}_2\text{CONH}_2)$, with water to produce carbon dioxide and ammonia. In water, without the enzyme, the reaction proceeds with a first-order rate constant of $4.15 \times 10^{-5} \text{ s}^{-1}$ at 100°C . In the presence of the enzyme in water, the reaction proceeds with a rate constant of $3.4 \times 10^4 \text{ s}^{-1}$ at 21°C . (a) Write out the balanced equation for the reaction catalyzed by urease. (b) If the rate of the catalyzed reaction were the same at 100°C as it is at 21°C , what would be the difference in the activation energy between the catalyzed and uncatalyzed reactions? (c) In actuality, what would you expect for the rate of the catalyzed reaction at 100°C as compared to that at 21°C ? (d) On the basis of parts (c) and (d), what can you conclude about the difference in activation energies for the catalyzed and uncatalyzed reactions?

14.46 Suppose that a certain biologically important reaction is quite slow at physiological temperature (37°C) in the absence of a catalyst. Assuming that the collision factor remains the same, by how much must an enzyme lower the activation energy of the reaction to achieve a 1×10^5 fold increase in the reaction rate?

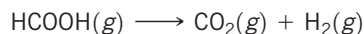
14.39 (b)

Answers to Self-Assessment Exercises

Sample Integrative Exercise

Putting Concepts Together

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:



The uncatalyzed decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 14.30. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.30.

- (a) Estimate the half-life and first-order rate constant for formic acid decomposition.
(b) What can you conclude from the effect of added ZnO on the decomposition of formic acid?
(c) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L . What effect would this have had on the calculated value of k ?

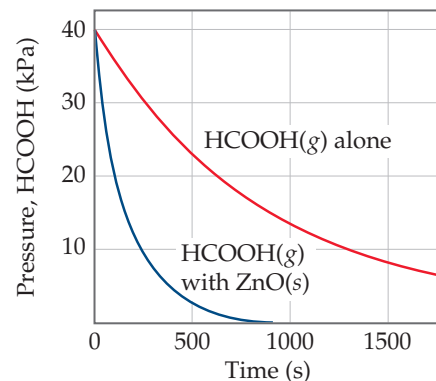


Figure 14.30 Variation in pressure of $\text{HCOOH}(g)$ as a function of time at 838 K .

- (d) The pressure of formic acid vapor at the start of the reaction is 40 kPa. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm³, how many moles of gas occupy the reaction chamber at the end of the reaction?
- (e) The standard heat of formation of formic acid vapor is $\Delta H_f^\circ = -378.6$ kJ/mol. Calculate ΔH° for the overall reaction. If the activation energy (E_a) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the reaction, and label E_a , ΔH° , and the transition state.

SOLUTION

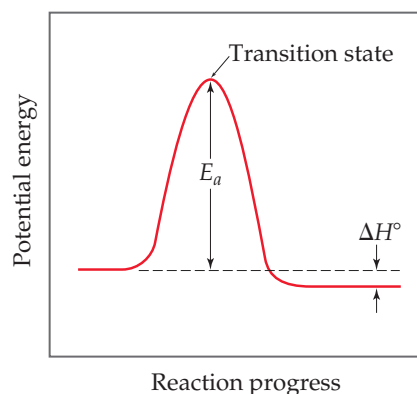
- (a) The initial pressure of HCOOH is 40 kPa. On the graph we move to the level at which the partial pressure of HCOOH is 20 kPa, half the initial value. This corresponds to a time of about 6.60×10^2 s, which is therefore the half-life. The first-order rate constant is given by Equation 14.17:
 $k = 0.693/t_{1/2} = 0.693/660 \text{ s} = 1.05 \times 10^{-3} \text{ s}^{-1}$.
- (b) The reaction proceeds much more rapidly in the presence of solid ZnO, so the surface of the oxide must be acting as a catalyst for the decomposition of the acid. This is an example of heterogeneous catalysis.
- (c) If we had graphed the concentration of formic acid in units of moles per liter, we would still have determined that the half-life for decomposition is 660 s, and we would have computed the same value for k . Because the units for k are s⁻¹, the value for k is independent of the units used for concentration.
- (d) According to the stoichiometry of the reaction, two moles of product are formed for each mole of reactant. When reaction is completed, therefore, the pressure will be 80 kPa, just twice the initial pressure, assuming ideal-gas behavior. (Because we are working at quite high temperature and fairly low gas pressure, assuming ideal-gas behavior is reasonable.) The number of moles of gas present can be calculated using the ideal-gas equation:

$$n = \frac{PV}{RT} = \frac{(80 \text{ kPa})(0.436 \text{ L})}{(8.314 \text{ m}^3 \text{ Pa/mol K})(838 \text{ K})} = 5.00 \times 10^{-3} \text{ mol}$$

- (e) We first calculate the overall change in energy, ΔH° , as in

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2(\text{g})) + \Delta H_f^\circ(\text{H}_2(\text{g})) - \Delta H_f^\circ(\text{HCOOH}(\text{g})) \\ &= -393.5 \text{ kJ/mol} + 0 - (-378.6 \text{ kJ/mol}) \\ &= -14.9 \text{ kJ/mol}\end{aligned}$$

From this and the given value for E_a , we can draw an approximate energy profile for the reaction, in analogy to Figure 14.16.



Chapter Summary and Key Terms

INTRODUCTION TO KINETICS (INTRODUCTION AND SECTION 14.1)

Chemical kinetics is the area of chemistry in which **reaction rates** are studied. Factors that affect reaction rate are the physical state of the reactants; concentration; temperature; and the presence of catalysts.

REACTION RATES (SECTION 14.2) Reaction rates are usually expressed as changes in concentration per unit time: Typically, for reactions in solution, rates are given in units of molarity per second (M/s). For most reactions, a plot of molarity versus time shows that the rate slows down as the reaction proceeds. The **instantaneous rate** is the slope of a line drawn tangent to the concentration-versus-time curve at a specific time. Rates can be written in terms of the appearance of products or the disappearance of reactants; the stoichiometry of the reaction dictates the relationship between rates of appearance and disappearance.

RATES AND CONCENTRATION (SECTION 14.3) The quantitative relationship between rate and concentration is expressed by a **rate law**, which usually has the following form:

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

The constant k in the rate law is called the **rate constant**; the exponents m , n , and so forth are called **reaction orders** for the reactants. The sum of the reaction orders gives the **overall reaction order**. Reaction orders must be determined experimentally. The units of the

rate constant depend on the overall reaction order. For a reaction in which the overall reaction order is 1, k has units of s⁻¹; for one in which the overall reaction order is 2, k has units of M⁻¹ s⁻¹.

Spectroscopy is one technique that can be used to monitor the course of a reaction. According to Beer's law, the absorption of electromagnetic radiation by a substance at a particular wavelength is directly proportional to its concentration.

CONCENTRATION AND TIME (SECTION 14.4) Rate laws can be used to determine the concentrations of reactants or products at any time during a reaction. In a **first-order reaction** the rate is proportional to the concentration of a single reactant raised to the first power: $\text{Rate} = k[A]$. In such cases the integrated form of the rate law is $\ln[A]_t = -kt + \ln[A]_0$, where $[A]_t$ is the concentration of reactant A at time t , k is the rate constant, and $[A]_0$ is the initial concentration of A. Thus, for a first-order reaction, a graph of $\ln[A]$ versus time yields a straight line of slope $-k$.

A **second-order reaction** is one for which the overall reaction order is 2. If a second-order rate law depends on the concentration of only one reactant, then $\text{rate} = k[A]^2$, and the time dependence of $[A]$ is given by the integrated form of the rate law: $1/[A]_t = 1/[A]_0 + kt$. In this case, a graph of $1/[A]_t$ versus time yields a straight line. A **zero-order reaction** is one for which the overall reaction order is 0. $\text{Rate} = k$ if the reaction is zero order.

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to drop to one-half of its original value. For a first-order reaction, the half-life depends only on the rate constant and not on the initial concentration: $t_{1/2} = 0.693/k$. The half-life of a second-order reaction depends on both the rate constant and the initial concentration of A: $t_{1/2} = 1/(k[A]_0)$.

THE EFFECT OF TEMPERATURE ON RATES (SECTION 14.5) The **collision model**, which assumes that reactions occur as a result of collisions between molecules, helps explain why the magnitudes of rate constants increase with increasing temperature. The greater the kinetic energy of the colliding molecules, the greater is the energy of collision. The minimum energy required for a reaction to occur is called the **activation energy**, E_a . A collision with energy E_a or greater can cause the atoms of the colliding molecules to reach the **activated complex** (or **transition state**), which is the highest energy arrangement in the pathway from reactants to products. Even if a collision is energetic enough, it may not lead to reaction; the reactants must also be correctly oriented relative to one another in order for a collision to be effective.

Because the kinetic energy of molecules depends on temperature, the rate constant of a reaction is very dependent on temperature. The relationship between k and temperature is given by the **Arrhenius equation**: $k = Ae^{-E_a/RT}$. The term A is called the **frequency factor**; it relates to the number of collisions that are favorably oriented for reaction. The Arrhenius equation is often used in logarithmic form: $\ln k = \ln A - E_a/RT$. Thus, a graph of $\ln k$ versus $1/T$ yields a straight line with slope $-E_a/R$.

REACTION MECHANISMS (SECTION 14.6) A **reaction mechanism** details the individual steps that occur in the course of a reaction. Each of these steps, called **elementary reactions**, has a well-defined rate law that depends on the number of molecules (the **molecularity**) of the step. Elementary reactions are defined as either **unimolecular**,

bimolecular, or **termolecular**, depending on whether one, two, or three reactant molecules are involved, respectively. Termolecular elementary reactions are very rare. Unimolecular, bimolecular, and termolecular reactions follow rate laws that are first order overall, second order overall, and third order overall, respectively.

Many reactions occur by a multistep mechanism, involving two or more elementary reactions, or steps. An **intermediate** is produced in one elementary step and is consumed in a later elementary step, therefore it does not appear in the overall equation for the reaction. When a mechanism has several elementary steps, the overall rate is limited by the slowest elementary step, called the **rate-determining step**. A fast elementary step that follows the rate-determining step will have no effect on the rate law of the reaction. A fast step that precedes the rate-determining step often creates an equilibrium that involves an intermediate. For a mechanism to be valid, the rate law predicted by the mechanism must be the same as that observed experimentally.

CATALYSTS (SECTION 14.7) A **catalyst** is a substance that increases the rate of a reaction without undergoing a net chemical change itself. It does so by providing a different mechanism for the reaction, one that has a lower activation energy. A **homogeneous catalyst** is one that is in the same phase as the reactants. A **heterogeneous catalyst** has a different phase from the reactants. Finely divided metals are often used as heterogeneous catalysts for solution- and gas-phase reactions. Reacting molecules can undergo binding, or **adsorption**, at the surface of the catalyst. The adsorption of a reactant at specific sites on the surface makes bond breaking easier, lowering the activation energy. Catalysis in living organisms is achieved by **enzymes**, large protein molecules that usually catalyze a very specific reaction. The specific reactant molecules involved in an enzymatic reaction are called **substrates**. The site of the enzyme where the catalysis occurs is called the **active site**. In the **lock-and-key model** for enzyme catalysis, substrate molecules bind very specifically to the active site of the enzyme, after which they can undergo reaction.

Learning Outcomes After studying this chapter, you should be able to:

- List the factors that affect the rate of chemical reactions. (Section 14.1) *Related Exercises: 14.2, 14.63*
- Determine the rate of a reaction by measuring the concentration of a reactant or product as a function of time. (Section 14.2) *Related Exercises: 14.5, 14.6, 14.64, 14.65*
- Relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction. (Section 14.2) *Related Exercises: 14.7, 14.8, 14.66, 14.67*
- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant. (Section 14.3) *Related Exercises: 14.11, 14.13, 14.68, 14.69*
- Determine the rate law and rate constant for a reaction from a series of experiments given the measured rates for various concentrations of reactants. (Section 14.3) *Related Exercises: 14.14, 14.15, 14.71, 14.72*
- Apply the integrated form of a rate law to determine the concentration of a reactant at a given time. (Section 14.4) *Related Exercises: 14.21, 14.75, 14.76*
- Apply the relationship between the rate constant of a first-order reaction and its half-life. (Section 14.4) *Related Exercises: 14.20, 14.75, 14.109, 14.110*
- Determine the order of a reaction from a table of reactant concentration as a function of time. (Section 14.4) *Related Exercises: 14.23, 14.24, 14.78, 14.79*
- Explain how the activation energy affects a rate and be able to use the Arrhenius equation. (Section 14.5) *Related Exercises: 14.31, 14.32, 14.84, 14.85*
- Predict a rate law for a reaction having a multistep mechanism given the individual steps in the mechanism. (Section 14.6) *Related Exercises: 14.37, 14.38, 14.90, 14.91*
- Explain the principles underlying catalysis. (Section 14.7) *Related Exercises: 14.40, 14.92–14.94*

Key Equations

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} \quad [14.4]$$

$$\text{Rate} = k[A]^m[B]^n \quad [14.7]$$

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln \frac{[A]_t}{[A]_0} = -kt \quad [14.12]$$

Definition of reaction rate in terms of the components of the balanced chemical equation $aA + bB \longrightarrow cC + dD$

General form of a rate law for the reaction $A + B \longrightarrow \text{products}$

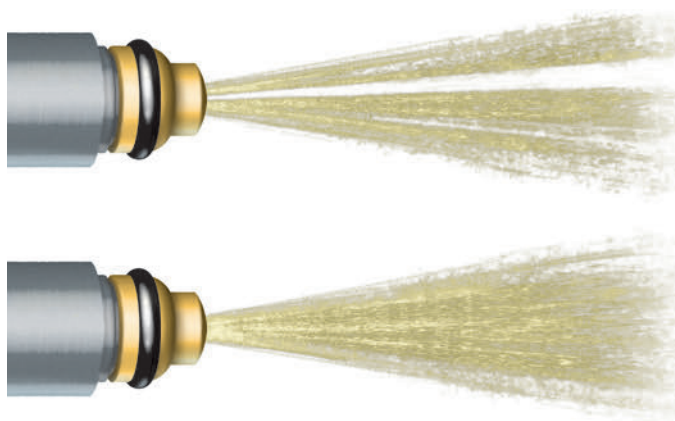
The integrated form of a first-order rate law for the reaction $A \longrightarrow \text{products}$

- $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ [14.14] The integrated form of a second-order rate law for the reaction $A \longrightarrow \text{products}$
- $[A]_t = -kt + [A]_0$ [14.16] The integrated form of a zero-order rate law for the reaction $A \longrightarrow \text{products}$
- $t_{1/2} = \frac{0.693}{k}$ [14.17] Relating the half-life and rate constant for a first-order reaction
- $k = Ae^{-E_a/RT}$ [14.21] The Arrhenius equation, which expresses how the rate constant depends on temperature
- $\ln k = -\frac{E_a}{RT} + \ln A$ [14.22] Logarithmic form of the Arrhenius equation

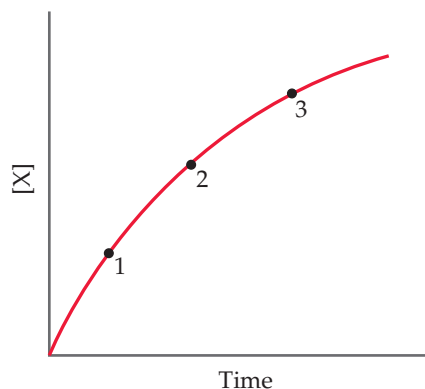
Exercises

Visualizing Concepts

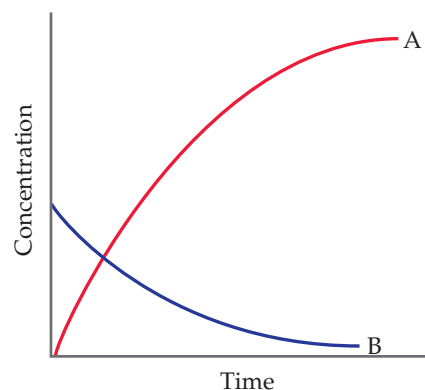
- 14.47** An automotive fuel injector dispenses a fine spray of gasoline into the automobile cylinder, as shown in the bottom drawing here. When an injector gets clogged, as shown in the top drawing, the spray is not as fine or even and the performance of the car declines. How is this observation related to chemical kinetics? [Section 14.1]



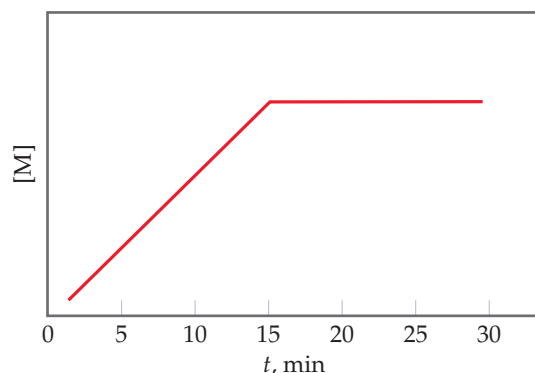
- 14.48** Consider the following graph of the concentration of a substance X over time. Is each of the following statements true or false? (a) X is a product of the reaction. (b) The rate of the reaction remains the same as time progresses. (c) The average rate between points 1 and 2 is greater than the average rate between points 1 and 3. (d) As time progresses, the curve will eventually turn downward toward the x-axis. [Section 14.2]



- 14.49** You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:

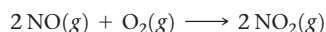


- (a) Which chemical equation is consistent with these data:
 (i) $A \longrightarrow B$, (ii) $B \longrightarrow A$, (iii) $A \longrightarrow 2B$,
 (iv) $B \longrightarrow 2A$?
- (b) Write equivalent expressions for the rate of the reaction in terms of the appearance or disappearance of the two substances. [Section 14.2]
- 14.50** Suppose that for the reaction $K + L \longrightarrow M$, you monitor the production of M over time, and then plot the following graph from your data:

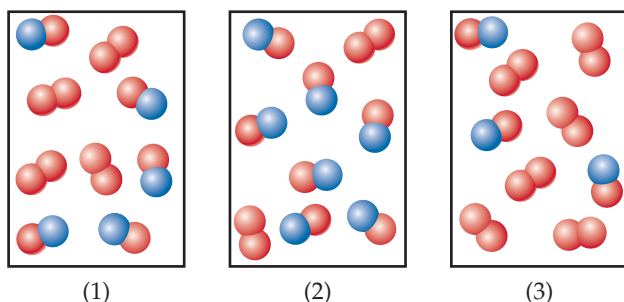


(a) From $t = 0$ to $t = 15$ min, what can you tell about the reaction rate? (b) How does the reaction change at $t = 15$ min? (c) Suppose the reaction as plotted here were started with 0.30 mol K and 0.40 mol L. After 20 min, an additional 0.10 mol K are added to the reaction mixture. Which of the following correctly describes how the plot would look from $t = 20$ min to $t = 30$ min? (i) $[M]$ would remain at the same constant value it has at $t = 20$ min, (ii) $[M]$ decreases and reaches 0 at $t = 25$ min, or (iii) $[M]$ would increase with the same slope as $t = 0$ to 15 min, until $t = 25$ min at which point the plot becomes horizontal again.

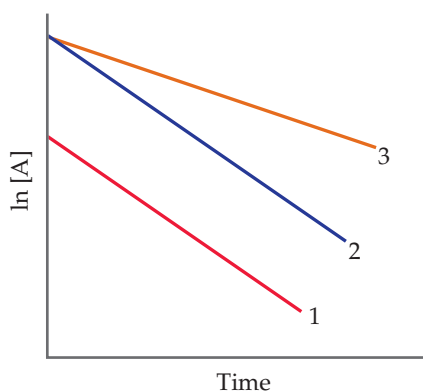
14.51 The following diagrams represent mixtures of $\text{NO}(g)$ and $\text{O}_2(g)$. These two substances react as follows:



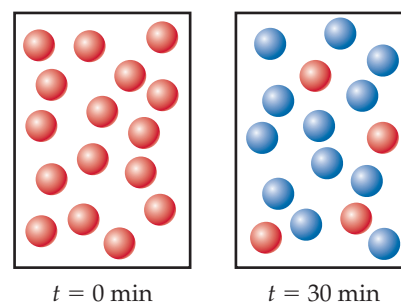
It has been determined experimentally that the rate is second order in NO and first order in O_2 . Based on this fact, which of the following mixtures will have the fastest initial rate? [Section 14.3]



14.52 A friend studies a first-order reaction and obtains the following three graphs for experiments done at two different temperatures. (a) Which two graphs represent experiments done at the same temperature? What accounts for the difference in these two graphs? In what way are they the same? (b) Which two graphs represent experiments done with the same starting concentration but at different temperatures? Which graph probably represents the lower temperature? How do you know? [Section 14.4]

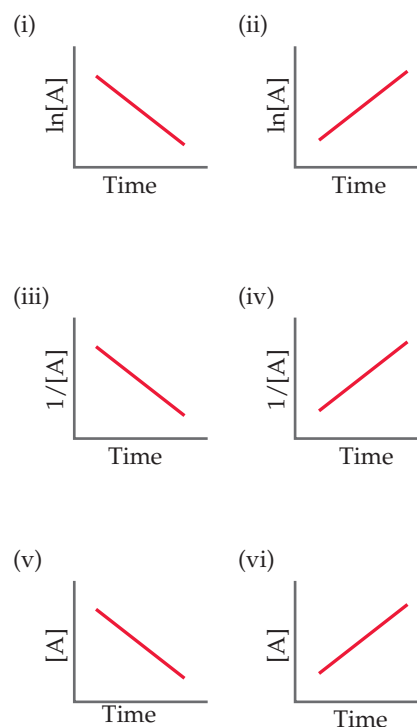


14.53 (a) Given the following diagrams at $t = 0$ min and $t = 30$ min, what is the half-life of the reaction if it follows first-order kinetics?

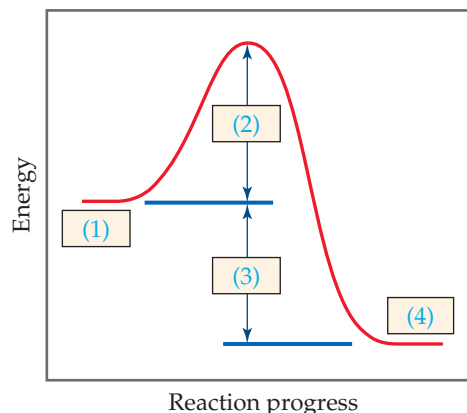


(b) After four half-life periods for a first-order reaction, what fraction of reactant remains? [Section 14.4]

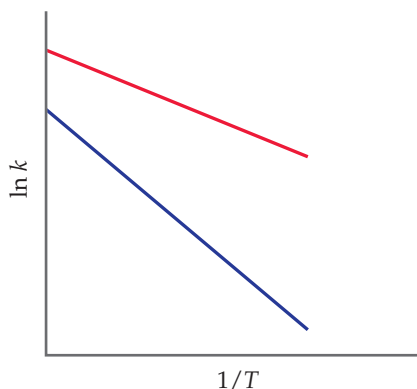
14.54 Which of the following linear plots do you expect for a reaction $A \longrightarrow \text{products}$ if the kinetics are (a) zero order, (b) first order, or (c) second order? [Section 14.4]



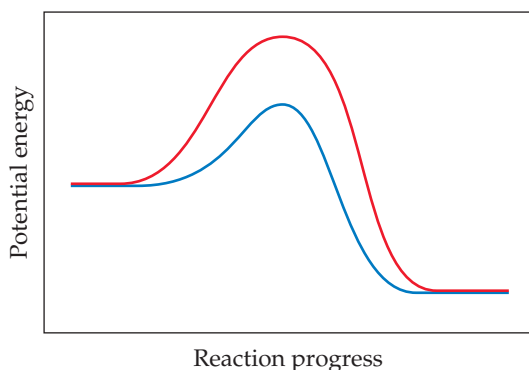
14.55 The following diagram shows a reaction profile. Label the components indicated by the boxes. [Section 14.5]



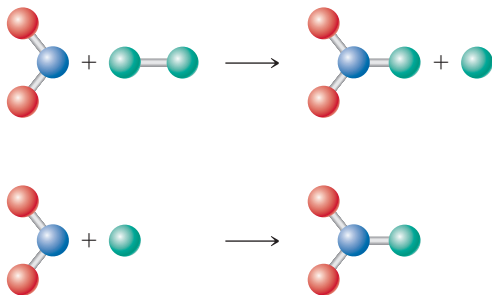
- 14.56** The accompanying graph shows plots of $\ln k$ versus $1/T$ for two different reactions. The plots have been extrapolated to the y -intercepts. Which reaction (red or blue) has (a) the larger value for E_a , and (b) the larger value for the frequency factor, A ? [Section 14.5]



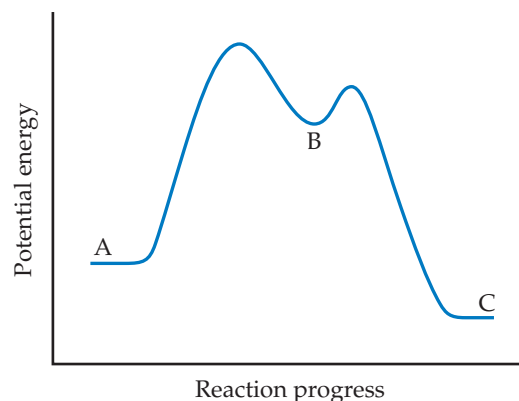
- 14.57** The following graph shows two different reaction pathways for the same overall reaction at the same temperature. Is each of the following statements true or false? (a) The rate is faster for the red path than for the blue path. (b) For both paths, the rate of the reverse reaction is slower than the rate of the forward reaction. (c) The energy change ΔE is the same for both paths. [Section 14.6]



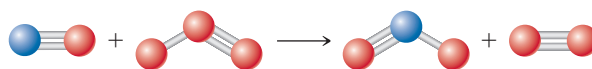
- 14.58** Consider the diagram that follows, which represents two steps in an overall reaction. The red spheres are oxygen, the blue ones nitrogen, and the green ones fluorine. (a) Write the chemical equation for each step in the reaction. (b) Write the equation for the overall reaction. (c) Identify the intermediate in the mechanism. (d) Write the rate law for the overall reaction if the first step is the slow, rate-determining step. [Section 14.6]



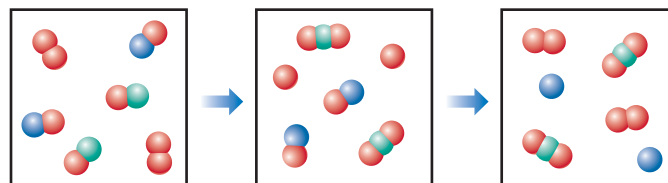
- 14.59** Based on the following reaction profile, how many intermediates are formed in the reaction $A \longrightarrow C$? How many transition states are there? Which step, $A \longrightarrow B$ or $B \longrightarrow C$, is the faster? For the reaction $A \longrightarrow C$, is ΔE positive, negative, or zero? [Section 14.6]



- 14.60** Draw a possible transition state for the bimolecular reaction depicted here. (The blue spheres are nitrogen atoms, and the red ones are oxygen atoms.) Use dashed lines to represent the bonds that are in the process of being broken or made in the transition state. [Section 14.6]



- 14.61** The following diagram represents an imaginary two-step mechanism. Let the red spheres represent element A, the green ones element B, and the blue ones element C. (a) Write the equation for the net reaction that is occurring. (b) Identify the intermediate. (c) Identify the catalyst. [Sections 14.6 and 14.7]



- 14.62** Draw a graph showing the reaction pathway for an overall exothermic reaction with two intermediates that are produced at different rates. On your graph indicate the reactants, products, intermediates, transition states, and activation energies. [Sections 14.6 and 14.7]

Reaction Rates (Sections 14.1 and 14.2)

- 14.63** (a) What are the units usually used to express the rates of reactions occurring in solution? (b) As the temperature increases, does the reaction rate increase or decrease? (c) As a reaction proceeds, does the instantaneous reaction rate increase or decrease?

- 14.64** Consider the following hypothetical aqueous reaction: $A(aq) \rightarrow B(aq)$. A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected:

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	0.031

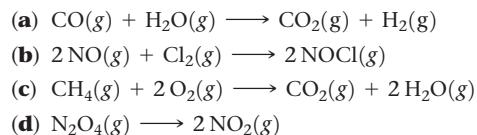
(a) Calculate the number of moles of B at each time in the table, assuming that there are no molecules of B at time zero and that A cleanly converts to B with no intermediates. (b) Calculate the average rate of disappearance of A for each 10 min interval in units of M/s . (c) Between $t = 0$ min and $t = 30$ min, what is the average rate of appearance of B in units of M/s ? Assume that the volume of the solution is constant.

- 14.65** The isomerization of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) was studied in the gas phase at $215^\circ C$, and the following data were obtained:

Time (s)	$[CH_3NC] (M)$
0	0.0165
2000	0.0110
5000	0.00591
8000	0.00314
12,000	0.00137
15,000	0.00074

(a) Calculate the average rate of reaction, in M/s , for the time interval between each measurement. (b) Calculate the average rate of reaction over the entire time of the data from $t = 0$ to $t = 15,000$ s. (c) Which is greater, the average rate between $t = 2000$ and $t = 12,000$ s, or between $t = 8000$ and $t = 15,000$ s? (d) Graph $[CH_3NC]$ versus time and determine the instantaneous rates in M/s at $t = 5000$ s and $t = 8000$ s.

- 14.66** For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the rate of appearance of each product:

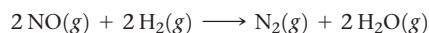


- 14.67** (a) Consider the combustion of hydrogen, $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$. If hydrogen is burning at a rate of 0.5 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor? (b) The reaction $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is carried out in a closed vessel. If the partial pressure of NO is decreasing at the rate of 60 kPa/min, what is the rate of change of the total pressure of the vessel?

Rate Laws (Section 14.3)

- 14.68** A reaction $A + B \longrightarrow C$ obeys the following rate law: $\text{Rate} = k[A]^3$. (a) If $[B]$ is doubled, how will the rate change? Will the rate constant change? (b) What are the reaction orders for A and B? What is the overall reaction order? (c) What are the units of the rate constant?

- 14.69** Consider the following reaction:



(a) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law. (b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4 M^{-2}s^{-1}$, what is the reaction rate when $[NO] = 0.035 M$ and $[H_2] = 0.015 M$? (c) What is the reaction rate at 1000 K when the concentration of NO is increased to $0.10 M$, while the concentration of H_2 is $0.010 M$? (d) What is the reaction rate at 1000 K if $[NO]$ is decreased to $0.010 M$ and $[H_2]$ is increased to $0.030 M$?

- 14.70** Consider the following reaction:



The rate law for this reaction is first order in C_2H_5Cl and first order in OH^- . When $[C_2H_5Cl] = 4.0 \times 10^{-3} M$ and $[OH^-] = 2.5 \times 10^{-2} M$, the reaction rate at 310 K is $5.20 \times 10^{-2} M/s$. (a) What is the value of the rate constant? (b) What are the units of the rate constant? (c) What would happen to the rate if the concentration of OH^- were cut in half? (d) What would happen to the rate if the concentration of both reactants were cut in half?

- 14.71** The iodide ion reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way: $OCl^- + I^- \longrightarrow OI^- + Cl^-$. This rapid reaction gives the following rate data:

$[OCl^-] (M)$	$[I^-] (M)$	Initial Rate (M/s)
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{-4}
3.0×10^{-3}	1.5×10^{-3}	2.72×10^{-4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{-4}

(a) Write the rate law for this reaction. (b) Calculate the rate constant with proper units. (c) Calculate the rate when $[OCl^-] = 2.0 \times 10^{-3} M$ and $[I^-] = 5.0 \times 10^{-4} M$.

- 14.72** The following data were measured for the reaction $BF_3(g) + NH_3(g) \longrightarrow F_3BNH_3(g)$:

Experiment	$[BF_3] (M)$	$[NH_3] (M)$	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

(a) What is the rate law for the reaction? (b) What is the overall order of the reaction? (c) Calculate the rate constant with proper units? (d) What is the rate when $[BF_3] = 0.100 M$ and $[NH_3] = 0.500 M$?

- 14.73** Consider the gas-phase reaction between nitric oxide and bromine at $273^\circ C$: $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$. The following data for the initial rate of appearance of NOBr were obtained:

Experiment	$[NO] (M)$	$[Br_2] (M)$	Initial Rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(a) Determine the rate law. (b) Calculate the average value of the rate constant for the appearance of NOBr from the four data sets. (c) How is the rate of appearance of NOBr related to the rate of disappearance of Br_2 ? (d) What is the rate of disappearance of Br_2 when $[NO] = 0.075 M$ and $[Br_2] = 0.25 M$?

Change of Concentration with Time (Section 14.4)

- 14.74** (a) Develop an equation for the half-life of a zero-order reaction. (b) Does the half-life of a zero-order reaction increase, decrease, or remain the same as the reaction proceeds?

- 14.75** Consider the reaction $2\text{C}_4\text{H}_6(\text{g}) \longrightarrow \text{C}_8\text{H}_{12}(\text{g})$, the rate constant at 500 K is $1.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and the initial concentration of A is 0.020 M. (a) What is the order of the reaction? (b) What is the half-life for this reaction? (c) How much $\text{C}_4\text{H}_6(\text{g})$ will remain after 1 hour at the same temperature?
- 14.76** The first-order rate constant for the decomposition of N_2O_5 , $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, at 70°C is $6.82 \times 10^{-3} \text{ s}^{-1}$. Suppose we start with 0.0250 mol of $\text{N}_2\text{O}_5(\text{g})$ in a volume of 2.0 L. (a) How many moles of N_2O_5 will remain after 5.0 min? (b) How many minutes will it take for the quantity of N_2O_5 to drop to 0.010 mol? (c) What is the half-life of N_2O_5 at 70°C ?
- 14.77** The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is first order in SO_2Cl_2 . Using the following kinetic data, determine the magnitude and units of the first-order rate constant:

Time (s)	Pressure SO_2Cl_2 (kPa)
0	101.3 kPa
2500	95.95 kPa
5000	90.69 kPa
7500	85.92 kPa
10,000	81.36 kPa

- 14.78** Consider the data in Exercise 14.64. (a) By using appropriate graphs, determine the reaction order with respect to A. (b) How long will it take to consume 90% of A initially present in the flask?
- 14.79** The gas-phase decomposition of NO_2 , $2\text{NO}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$, is studied at 383°C , giving the following data:

Time (s)	$[\text{NO}_2]$ (M)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

(a) Is the reaction first order or second order with respect to the concentration of NO_2 ? (b) What is the rate constant? (c) Predict the reaction rates at the beginning of the reaction for initial concentrations of 0.200 M, 0.100 M, and 0.050 M NO_2 .

Temperature and Rate (Section 14.5)

- 14.80** (a) In which of the following reactions would you expect the orientation factor to be more important in leading to reaction: $\text{O}_3 + \text{O} \longrightarrow 2\text{O}_2$ or $\text{NO} + \text{NO}_3 \longrightarrow 2\text{NO}_2$? (b) What is related to the orientation factor? Which, smaller or larger ratio of effectively oriented collisions to all possible collisions, would lead to a smaller orientation factor?
- 14.81** Calculate the fraction of molecules in a sample of nitro gas at 300 K that has an energy of 10.0 kJ or greater.
- 14.82** The gas-phase reaction $\text{Cl}(\text{g}) + \text{HBr}(\text{g}) \longrightarrow \text{HCl}(\text{g}) + \text{Br}(\text{g})$ has an overall energy change of -66 kJ . The activation energy for the reaction is 7 kJ. (a) Sketch the energy profile for the reaction, and label E_a and ΔE . (b) What is the activation energy for the reverse reaction?
- 14.83** Indicate whether each statement is true or false.
- (a) If you compare two reactions with similar collision factors, the one with the larger activation energy will be faster.

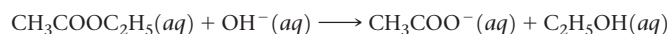
- (b) A reaction that has a small rate constant must have a small frequency factor.
- (c) Increasing the reaction temperature increases the fraction of successful collisions between reactants.

14.84 Based on their activation energies and energy changes and assuming that all collision factors are the same, rank the following reactions from slowest to fastest.

- (a) $E_a = 75 \text{ kJ/mol}$; $\Delta E = -20 \text{ kJ/mol}$
 (b) $E_a = 100 \text{ kJ/mol}$; $\Delta E = +30 \text{ kJ/mol}$
 (c) $E_a = 85 \text{ kJ/mol}$; $\Delta E = -50 \text{ kJ/mol}$

14.85 (a) A certain first-order reaction has a rate constant of $2.75 \times 10^{-2} \text{ s}^{-1}$ at 20°C . What is the value of k at 60°C if $E_a = 75.5 \text{ kJ/mol}$? (b) Another first-order reaction also has a rate constant of $2.75 \times 10^{-2} \text{ s}^{-1}$ at 20°C . What is the value of k at 60°C if $E_a = 125 \text{ kJ/mol}$? (c) What assumptions do you need to make in order to calculate answers for parts (a) and (b)?

14.86 The rate of the reaction



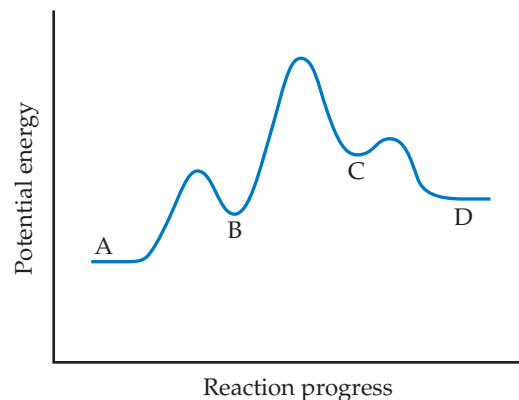
was measured at several temperatures, and the following data were collected:

Temperature ($^\circ\text{C}$)	k ($\text{M}^{-1} \text{ s}^{-1}$)
15	0.0521
25	0.101
35	0.184
45	0.332

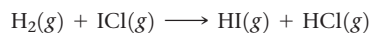
Calculate the value of E_a by constructing an appropriate graph.

Reaction Mechanisms (Section 14.6)

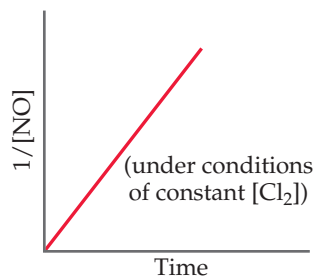
- 14.87** (a) What is meant by the term *elementary reaction*? (b) What is the difference between a *unimolecular* and a *bimolecular* elementary reaction? (c) What is a *reaction mechanism*? (d) What is meant by the term *rate-determining step*?
- 14.88** What is the molecularity of each of the following elementary reactions? Write the rate law for each.
- (a) $\text{H}_2\text{O}(\text{l}) + \text{CN}^-(\text{aq}) \longrightarrow \text{HCN}(\text{aq})$
 (b) $\text{CH}_3\text{Cl}(\text{soln}) + \text{OH}^-(\text{soln}) \longrightarrow \text{CH}_3\text{OH}(\text{soln}) + \text{Cl}^-(\text{soln})$
 (c) $\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2\text{NO}_2$
- 14.89** (a) Based on the following reaction profile, how many intermediates are formed in the reaction $\text{A} \longrightarrow \text{D}$? (b) How many transition states are there? (c) Which step is the fastest? (d) For the reaction $\text{A} \longrightarrow \text{D}$, is ΔE positive, negative, or zero?



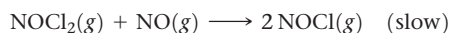
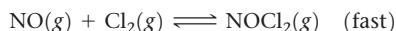
- 14.90** The following mechanism has been proposed for the gas-phase reaction of H_2 with ICl :



- (a) Write the balanced equation for the overall reaction. (b) Identify any intermediates in the mechanism. (c) If the first step is slow and the second one is fast, which rate law do you expect to be observed for the overall reaction?
- 14.91** The reaction $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{NOCl}(\text{g})$ was performed and the following data were obtained under conditions of constant $[\text{Cl}_2]$:



- (a) Is the following mechanism consistent with the data?



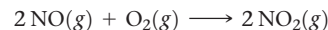
- (b) Does the linear plot guarantee that the overall rate law is second order?

Catalysis (Section 14.7)

- 14.92** (a) What is a catalyst? (b) What is the difference between a homogeneous and a heterogeneous catalyst? (c) Do catalysts affect the overall enthalpy change for a reaction, the activation energy, or both?
- 14.93** In Figure 14.21, we saw that $\text{Br}^-(\text{aq})$ catalyzes the decomposition of $\text{H}_2\text{O}_2(\text{aq})$ into $\text{H}_2\text{O}(\text{l})$ and $\text{O}_2(\text{g})$. Suppose that some $\text{KBr}(\text{s})$ is added to an aqueous solution of hydrogen

peroxide. Make a sketch of $[\text{Br}^-(\text{aq})]$ versus time from the addition of the solid to the end of the reaction.

- 14.94** The oxidation of SO_2 to SO_3 is accelerated by NO_2 . The reaction proceeds according to:



(a) Show that, with appropriate coefficients, the two reactions can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3 . (b) Do we consider NO_2 a catalyst or an intermediate in this reaction? (c) Would you classify NO as a catalyst or as an intermediate? (d) Is this an example of homogeneous catalysis or heterogeneous catalysis?

- 14.95** Many metallic catalysts, particularly the precious-metal ones, are often deposited as very thin films on a substance of high surface area per unit mass, such as alumina (Al_2O_3) or silica (SiO_2). (a) Why is this an effective way of utilizing the catalyst material compared to having powdered metals? (b) How does the surface area affect the rate of reaction?

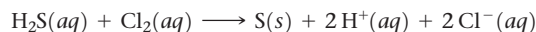
- 14.96** When D_2 reacts with ethene (C_2H_4) in the presence of a finely divided catalyst, ethane with two deuteriums, $\text{CH}_3\text{D}-\text{CH}_2\text{D}$, is formed. (Deuterium, D, is an isotope of hydrogen of mass 2.) Very little ethane forms in which two deuteriums are bound to one carbon (for example, CH_3-CHD_2). Use the sequence of steps involved in the reaction (Figure 14.23) to explain why this is so.

- 14.97** A certain enzyme catalyzes a biochemical reaction. In water, without the enzyme, the reaction proceeds with a rate constant of $6.50 \times 10^{-4} \text{ min}^{-1}$ at 37°C . In the presence of the enzyme in water, the reaction proceeds with a rate constant of $1.67 \times 10^4 \text{ min}^{-1}$ at 37°C . Assuming the collision factor is the same for both situations, calculate the difference in activation energies for the uncatalyzed versus enzyme-catalyzed reaction.

- 14.98** The activation energy of an uncatalyzed reaction is 95 kJ/mol . The addition of a catalyst lowers the activation energy to 55 kJ/mol . Assuming that the collision factor remains the same, by what factor will the catalyst increase the rate of the reaction at (a) 25°C , (b) 125°C ?

Additional Exercises

- 14.99** Consider the reaction $2\text{A} \longrightarrow \text{B}$. Is each of the following statements true or false? (a) The rate law for the reaction must be, $\text{Rate} = k[\text{A}]^2$. (b) If the reaction is an elementary reaction, the rate law is second order. (c) If the reaction is an elementary reaction, the rate law of the reverse reaction is first order. (d) The activation energy for the reverse reaction must be smaller than that for the forward reaction.
- 14.100** Hydrogen sulfide (H_2S) is a common and troublesome pollutant in industrial wastewaters. One way to remove H_2S is to treat the water with chlorine, in which case the following reaction occurs:

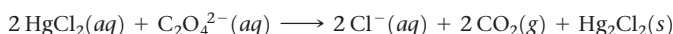


The rate of this reaction is first order in each reactant. The rate constant for the disappearance of H_2S at 30°C is $4.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. If at a given time the concentration of H_2S is $2.5 \times 10^{-4} \text{ M}$ and that of Cl_2 is $2.0 \times 10^{-2} \text{ M}$, what is the rate of formation of H^+ ?

- 14.101** The reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ is second order in NO and first order in O_2 . When $[\text{NO}] = 0.040 \text{ M}$, and $[\text{O}_2] = 0.035 \text{ M}$, the observed rate of disappearance of NO is $9.3 \times 10^{-5} \text{ M/s}$. (a) What is the rate of disappearance of O_2 at this moment? (b) What is the value of the rate constant? (c) What are the units of the rate constant? (d) What would happen to the rate if the concentration of NO were increased by a factor of 1.8?

- 14.102** You perform a series of experiments for the reaction $\text{A} \rightarrow 2\text{B}$ and find that the rate law has the form, $\text{rate} = k[\text{A}]^x$. Determine the value of x in each of the following cases: (a) The rate increases by a factor of 6.25, when $[\text{A}]_0$ is increased by a factor of 2.5. (b) There is no rate change when $[\text{A}]_0$ is increased by a factor of 4. (c) The rate decreases by a factor of $1/2$, when $[\text{A}]_0$ is cut in half.

- 14.103** Consider the following reaction between mercury(II) chloride and oxalate ion:



The initial rate of this reaction was determined for several concentrations of HgCl_2 and $\text{C}_2\text{O}_4^{2-}$, and the following rate data were obtained for the rate of disappearance of $\text{C}_2\text{O}_4^{2-}$:

Experiment	$[\text{HgCl}_2] (M)$	$[\text{C}_2\text{O}_4^{2-}] (M)$	Rate (M/s)
1	0.164	0.15	3.2×10^{-5}
2	0.164	0.45	2.9×10^{-4}
3	0.082	0.45	1.4×10^{-4}
4	0.246	0.15	4.8×10^{-5}

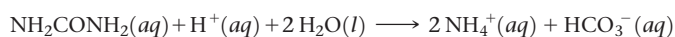
(a) What is the rate law for this reaction? (b) What is the value of the rate constant with proper units? (c) What is the reaction rate when the initial concentration of HgCl_2 is $0.100 M$ and that of $\text{C}_2\text{O}_4^{2-}$ is $0.25 M$ if the temperature is the same as that used to obtain the data shown?

- 14.104** The following kinetic data are collected for the initial rates of a reaction $2 X + Z \longrightarrow \text{products}$:

Experiment	$[X]_0 (M)$	$[Z]_0 (M)$	Rate (M/s)
1	0.25	0.25	4.0×10^1
2	0.50	0.50	3.2×10^2
3	0.50	0.75	7.2×10^2

(a) What is the rate law for this reaction? (b) What is the value of the rate constant with proper units? (c) What is the reaction rate when the initial concentration of X is $0.75 M$ and that of Z is $1.25 M$?

- 14.105** The dimerization of C_2F_4 to C_4F_8 has a rate constant $k = 0.045 M^{-1}s^{-1}$ at $450 K$. (a) Based on the unit of k , what is the reaction order in C_2F_4 ? (b) If the initial concentration of C_2F_4 is $0.100 M$, how long would it take for the concentration to decrease to $0.020 M$ at $450 K$?
- 14.106** Consider two reactions. Reaction (1) has a half-life that gets longer as the reaction proceeds. Reaction (2) has a half-life that gets shorter as the reaction proceeds. What can you conclude about the rate laws of these reactions from these observations?
- 14.107** For a first order reaction $A \longrightarrow B + C$, if the half-life of A at 25°C is $3.05 \times 10^4 s$, what is the rate constant k at this temperature? What percentage of A will not have reacted after one day?
- 14.108** (a) The reaction $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(aq) + \text{C}_6\text{H}_{12}\text{O}_6(aq)$ is first order with in $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$ and zero-order in H_2O . At $300 K$ the rate constant equals $3.30 \times 10^{-2} \text{min}^{-1}$. Calculate the half-life at this temperature. (b) If the activation energy for this reaction is 80.0 kJ/mol , at what temperature would the reaction rate be doubled?
- 14.109** Cobalt-60 is used in radiation therapy to treat cancer. It has a first-order rate constant for radioactive decay of $k = 1.31 \times 10^{-1} \text{yr}^{-1}$. Another radioactive isotope, iron-59, which is used as a tracer in the study of iron metabolism, has a rate constant of $k = 1.55 \times 10^{-2} \text{day}^{-1}$. (a) What are the half-lives of these two isotopes? (b) Which one decays at a faster rate? (c) How much of a 1.00 mg sample of each isotope remains after three half-lives? How much of a 1.00 mg sample of each isotope remains after five days?
- 14.110** Urea (NH_2CONH_2) is the end product in protein metabolism in animals. The decomposition of urea in $0.1 M \text{HCl}$ occurs according to the reaction



The reaction is first order in urea and first order overall. When $[\text{NH}_2\text{CONH}_2] = 0.200 M$, the rate at 61.05°C is $8.56 \times 10^{-5} M/s$. (a) What is the rate constant, k ? (b) What is the concentration of urea in this solution after $4.00 \times 10^3 s$ if the starting concentration is $0.500 M$? (c) What is the half-life for this reaction at 61.05°C ?

- 14.111** The rate of a first-order reaction is followed by spectroscopy, monitoring the absorbance of a colored reactant at 520 nm . The reaction occurs in a 1.00 cm sample cell, and the only colored species in the reaction has an extinction coefficient of $5.60 \times 10^3 M^{-1} \text{cm}^{-1}$ at 520 nm . (a) Calculate the initial concentration of the colored reactant if the absorbance is 0.605 at the beginning of the reaction. (b) The absorbance falls to 0.250 at 30.0 min . Calculate the rate constant in units of s^{-1} . (c) Calculate the half-life of the reaction. (d) How long does it take for the absorbance to fall to 0.100 ?
- 14.112** A colored dye compound decomposes to give a colorless product. The original dye absorbs at 608 nm and has an extinction coefficient of $4.7 \times 10^4 M^{-1} \text{cm}^{-1}$ at that wavelength. You perform the decomposition reaction in a 1-cm cuvette in a spectrometer and obtain the following data:

Time (min)	Absorbance at 608 nm
0	1.254
30	0.941
60	0.752
90	0.672
120	0.545

From these data, determine the rate law for the reaction "dye $\longrightarrow$ product" and determine the rate constant.

- 14.113** Cyclopentadiene (C_5H_6) reacts with itself to form dicyclopentadiene ($\text{C}_{10}\text{H}_{12}$). A $0.0400 M$ solution of C_5H_6 was monitored as a function of time as the reaction $2 \text{C}_5\text{H}_6 \longrightarrow \text{C}_{10}\text{H}_{12}$ proceeded. The following data were collected:

Time (s)	$[\text{C}_5\text{H}_6] (M)$
0.0	0.0400
50.0	0.0300
100.0	0.0240
150.0	0.0200
200.0	0.0174

Plot $[\text{C}_5\text{H}_6]$ versus time, $\ln[\text{C}_5\text{H}_6]$ versus time, and $1/[\text{C}_5\text{H}_6]$ versus time. (a) What is the order of the reaction? (b) What is the value of the rate constant?

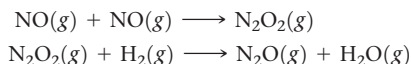
- 14.114** The first-order rate constant for reaction of a particular organic compound with water varies with temperature as follows:

Temperature (K)	Rate Constant (s^{-1})
300	3.2×10^{-11}
320	1.0×10^{-9}
340	3.0×10^{-8}
355	2.4×10^{-7}

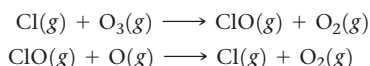
From these data, calculate the activation energy in units of kJ/mol .

- 14.115** At 25°C , raw milk sours in 6.0 h but takes 60 h to sour in a refrigerator at 5°C . Estimate the activation energy in kJ/mol for the reaction that leads to the souring of milk.

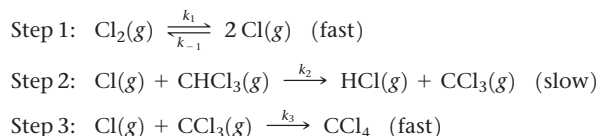
- 14.116** The following mechanism has been proposed for the reaction of NO with H₂ to form N₂O and H₂O:



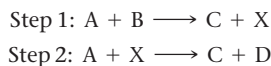
- (a) Show that the elementary reactions of the proposed mechanism add to provide a balanced equation for the reaction. (b) Write a rate law for each elementary reaction in the mechanism. (c) Identify any intermediates in the mechanism. (d) The observed rate law is $\text{rate} = k[\text{NO}]^2[\text{H}_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second reactions?
- 14.117** Ozone in the upper atmosphere can be destroyed by the following two-step mechanism:



- (a) What is the overall equation for this process? (b) What is the catalyst in the reaction? (c) What is the intermediate in the reaction?
- 14.118** The gas-phase decomposition of ozone is thought to occur by the following two-step mechanism.
- Step 1: $\text{O}_3(g) \rightleftharpoons \text{O}_2(g) + \text{O}(g)$ (fast)
- Step 2: $\text{O}(g) + \text{O}_3(g) \longrightarrow 2\text{O}_2(g)$ (slow)
- (a) Write the balanced equation for the overall reaction. (b) Derive the rate law that is consistent with this mechanism. (*Hint*: The product appears in the rate law.) (c) Is O a catalyst or an intermediate? (d) If instead the reaction occurred in a single step, would the rate law change? If so, what would it be?
- 14.119** The following mechanism has been proposed for the gas-phase reaction of chloroform (CHCl₃) and chlorine:



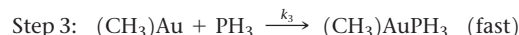
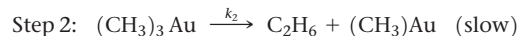
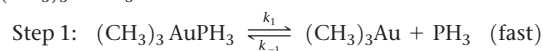
- (a) What is the overall reaction? (b) What are the intermediates in the mechanism? (c) What is the molecularity of each of the elementary reactions? (d) What is the rate-determining step? (e) What is the rate law predicted by this mechanism? (*Hint*: The overall reaction order is not an integer.)
- 14.120** Consider the hypothetical reaction $2\text{A} + \text{B} \longrightarrow 2\text{C} + \text{D}$. The following two-step mechanism is proposed for the reaction:



X is an unstable intermediate. (a) What is the predicted rate law expression if Step 1 is rate determining? (b) What is the predicted rate law expression if Step 2 is rate determining? (c) Your result for part (b) might be considered surprising for which of the following reasons: (i) The concentration of a product is in the rate law. (ii) There is a negative reaction order in the rate law. (iii) Both reasons (i) and (ii). (iv) Neither reasons (i) nor (ii).

- 14.121** In a hydrocarbon solution, the gold compound (CH₃)₃AuPH₃ decomposes into ethane (C₂H₆) and a

different gold compound, (CH₃)AuPH₃. The following mechanism has been proposed for the decomposition of (CH₃)₃AuPH₃:



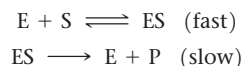
(a) What is the overall reaction? (b) What are the intermediates in the mechanism? (c) What is the molecularity of each of the elementary steps? (d) What is the rate-determining step? (e) What is the rate law predicted by this mechanism? (f) What would be the effect on the reaction rate of adding PH₃ to the solution of (CH₃)₃AuPH₃?

- 14.122** Platinum nanoparticles of diameter ~2 nm are important catalysts in carbon monoxide oxidation to carbon dioxide. Platinum crystallizes in a face-centered cubic arrangement with an edge length of 392.4 pm. (a) Estimate how many platinum atoms would fit into a 2.0-nm sphere; the volume of a sphere is $(4/3)\pi r^3$. Recall that 1 pm = 1×10^{-12} m and 1 nm = 1×10^{-9} m. (b) Estimate how many platinum atoms are on the surface of a 2.0-nm Pt sphere, using the surface area of a sphere ($4\pi r^2$) and assuming that the “footprint” of one Pt atom can be estimated from its atomic diameter of 280 pm. (c) Using your results from (a) and (b), calculate the percentage of Pt atoms that are on the surface of a 2.0-nm nanoparticle. (d) Repeat these calculations for a 5.0-nm platinum nanoparticle. (e) Which size of nanoparticle would you expect to be more catalytically active and why?

- 14.123** The human body is characterized by an extremely complex system of interrelated chemical reactions. A large number of enzymes are necessary for many of these reactions to occur at suitable rates. Enzymes are very selective in the reactions they catalyze, and some are absolutely specific. Use the lock-and-key model to account for the specificity of an enzyme.

- 14.124** Suppose that, in the absence of a catalyst, a certain biochemical reaction occurs x times per second at normal body temperature (37 °C). In order to be physiologically useful, the reaction needs to occur 5000 times faster than when it is uncatalyzed. By how many kJ/mol must an enzyme lower the activation energy of the reaction to make it useful?

- 14.125** Enzymes are often described as following the two-step mechanism:



where E = enzyme, S = substrate,

ES = enzyme–substrate complex, and P = product.

(a) If an enzyme follows this mechanism, what rate law is expected for the reaction? (b) Molecules that can bind to the active site of an enzyme but are not converted into product are called *enzyme inhibitors*. Write an additional elementary step to add into the preceding mechanism to account for the reaction of E with I, an inhibitor.

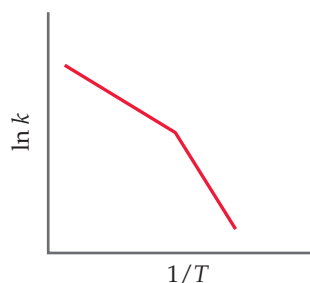
Integrative Exercises

- 14.126** The rate of the reaction $4 \text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6 \text{H}_2(\text{g})$ was studied by charging $\text{PH}_3(\text{g})$ into a constant-volume reaction vessel and measuring the total pressure.

Time (s)	0	30	60	90	120
P_{total} (kPa)	13.3	18.5	20.9	22.1	22.8

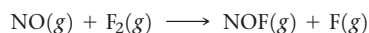
Determine the reaction order and also the rate constant for the reaction.

- 14.127** The reaction between ethyl iodide and hydroxide ion in ethanol ($\text{C}_2\text{H}_5\text{OH}$) solution, $\text{C}_2\text{H}_5\text{I}(\text{alc}) + \text{OH}^-(\text{alc}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{I}^-(\text{alc})$ has an activation energy of 86.8 kJ/mol and a frequency factor of $2.1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. (a) Predict the rate constant for the reaction at 30°C . (b) A solution of KOH in ethanol is made up by dissolving 0.500 g KOH in ethanol to form 500 mL of solution. Similarly, 1.500 g of $\text{C}_2\text{H}_5\text{I}$ is dissolved in ethanol to form 500 mL of solution. Equal volumes of the two solutions are mixed. Assuming the reaction is first order in each reactant, what is the initial rate at 30°C ? (c) Which reagent in the reaction is limiting, assuming the reaction proceeds to completion? (d) Assuming the frequency factor and activation energy do not change as a function of temperature, calculate the rate constant for the reaction at 40°C .
- 14.128** You obtain kinetic data for a reaction at a set of different temperatures. You plot $\ln k$ versus $1/T$ and obtain the following graph:



Suggest a molecular-level interpretation of these unusual data.

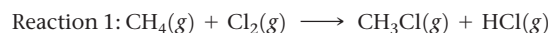
- 14.129** The gas-phase reaction of NO with F_2 to form NOF and F has an activation energy of $E_a = 6.3 \text{ kJ/mol}$, and a frequency factor of $A = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The reaction is believed to be bimolecular:



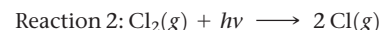
- (a) Calculate the rate constant at 100°C . (b) Draw the Lewis structures for the NO and the NOF molecules, given that the chemical formula for NOF is misleading because the nitrogen atom is actually the central atom in the molecule. (c) Predict the shape for the NOF molecule. (d) Draw a possible transition state for the formation of NOF, using dashed lines to indicate the weak bonds that are beginning to form. (e) Suggest a reason for the low activation energy for the reaction.
- 14.130** The mechanism for the oxidation of HBr by O_2 to form $2 \text{H}_2\text{O}$ and Br_2 is shown in Exercise 14.38. (a) Calculate the overall standard enthalpy change for the reaction process. (b) HBr does not react with O_2 at a measurable rate at room temperature under ordinary conditions. What can you infer from this about the magnitude of the activation energy for the rate-determining step? (c) Draw a plausible Lewis structure for the intermediate HOOBr . To

what familiar compound of hydrogen and oxygen does it appear similar?

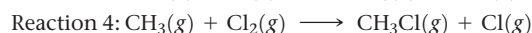
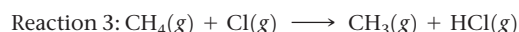
- 14.131** The rates of many atmospheric reactions are accelerated by the absorption of light by one of the reactants. For example, consider the reaction between methane and chlorine to produce methyl chloride and hydrogen chloride:



This reaction is very slow in the absence of light. However, $\text{Cl}_2(\text{g})$ can absorb light to form Cl atoms:



Once the Cl atoms are generated, they can catalyze the reaction of CH_4 and Cl_2 , according to the following proposed mechanism:



The enthalpy changes and activation energies for these two reactions are tabulated as follows:

Reaction	ΔH° (kJ/mol)	E_a (kJ/mol)
3	+4	17
4	-109	4

- (a) By using the bond enthalpy for Cl_2 (Table 8.4), determine the longest wavelength of light that is energetic enough to cause reaction 2 to occur. In which portion of the electromagnetic spectrum is this light found? (b) By using the data tabulated here, sketch a quantitative energy profile for the catalyzed reaction represented by reactions 3 and 4. (c) By using bond enthalpies, estimate where the reactants, $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g})$, should be placed on your diagram in part (b). Use this result to estimate the value of E_a for the reaction $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3(\text{g}) + \text{HCl}(\text{g}) + \text{Cl}(\text{g})$. (d) The species $\text{Cl}(\text{g})$ and $\text{CH}_3(\text{g})$ in reactions 3 and 4 are radicals, that is, atoms or molecules with unpaired electrons. Draw a Lewis structure of CH_3 , and verify that it is a radical. (e) The sequence of reactions 3 and 4 comprises a radical chain mechanism. Why do you think this is called a “chain reaction”? Propose a reaction that will terminate the chain reaction.

- 14.132** Many primary amines, RNH_2 , where R is a carbon-containing fragment such as CH_3 , CH_3CH_2 , and so on, undergo reactions where the transition state is tetrahedral. (a) Draw a hybrid orbital picture to visualize the bonding at the nitrogen in a primary amine (just use a C atom for “R”). (b) What kind of reactant with a primary amine can produce a tetrahedral intermediate?

- 14.133** The NO_x waste stream from automobile exhaust includes species such as NO and NO_2 . Catalysts that convert these species to N_2 are desirable to reduce air pollution. (a) Draw the Lewis dot and VSEPR structures of NO, NO_2 , and N_2 . (b) Using a resource such as Table 8.3, look up the energies of the bonds in these molecules. In what region of the electromagnetic spectrum are these energies? (c) Design a spectroscopic experiment to monitor the conversion of NO_x into N_2 , describing what wavelengths of light need to be monitored as a function of time.

- 14.134** As shown in Figure 14.23, the first step in the heterogeneous hydrogenation of ethene is adsorption of the ethene molecule on a metal surface. One proposed